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especially when dealing with volatile substances. The combustion takes 40—50 minutes, including the time (20 minutes) required to drive off the water formed; the absorption tubes are then detached, and weighed after 20 minutes.

The following precautions are essential: (1) a sufficient supply of oxygen must be maintained, the outer stream at the rate of two bubbles a second with a bubble-counter 1 mm. in diameter; (2) a good analysis can be obtained only after a satisfactory blank or a successful combustion. Otherwise the process requires no special care. The progress of the combustion can be watched so that any irregularity is noticed at once, the filling of the tube is simple, and the large absorption tubes do not require refilling for a considerable time.

We obtained consistently high results in the estimation of nitrogen by Pregl's method until we placed the layer of reduced copper at the end of the tube as in Dubsky's process; this arrangement obviated the dissociation of the carbon dioxide into carbon monoxide and oxygen. A very slow stream of carbon dioxide generated in a Kipp apparatus was maintained throughout the combustion; and no difficulty was experienced in getting air-free carbon dioxide when Pregl's directions for the filling of the Kipp apparatus were carefully followed.—STATE SCHOOL OF HYGIENE, WARSAW, POLAND. [*Received, April 15th*, 1925.]

CCXXXIII.—*Arylselenoglycollic Acids.*

By GILBERT T. MORGAN and WILLIAM HENRY PORRITT.

ARYLSELENOGLYCOLLIC acids are obtainable by the following process, which avoids the use of hydrogen selenide and is of general application. The first step, due to Taboury (*Bull. Soc. chim.*, 1903, **29**, 761), depends on the interaction of elemental selenium and a magnesium aryl bromide.

The additive product of the Grignard reagent and selenium is decomposed with ice and hydrochloric acid, and the arylselenomercaptan, extracted as alkali salt from its ethereal solution, is condensed with sodium chloroacetate in aqueous alcoholic solution. The process is summarised in the following scheme:

$$\text{Aryl·MgBr} \longrightarrow \text{Aryl·Se·MgBr} \longrightarrow \text{Aryl·SeH}.$$

$$\text{Aryl·SeNa} + \text{CH}_2\text{Cl·CO}_2\text{Na} = \text{Aryl·Se·CH}_2\text{·CO}_2\text{Na} + \text{NaCl}.$$

During its extraction with aqueous alkali 15—20% of the selenomercaptan undergoes aerial oxidation to the corresponding diaryl diselenide, Aryl·Se·Se·Aryl.

The arylselenoglycollic acids (yields 20—25%), when liberated

by mineral acids from their alkali salts, are well-defined, colourless solids, easily soluble in organic media, crystallising from hot water on account of their more sparing solubility in the cold solvent.

In general stability, the arylselenoglycollic acids resemble their sulphur analogues; they melt without decomposition and are not attacked by boiling mineral acids. Unlike the acids of the sulphur series, however, these selenium derivatives do not exhibit any marked tendency towards ring formation under the influence of chlorosulphonic acid at temperatures ranging from −5° to 40°. No seleno-indoxylic substances are produced and the products isolated resemble the decomposition products of the dichlorides of the arylselenoglycollic acids. This observation indicates that the chlorosulphonic acid contributes chlorine to the side chain, which radical subsequently undergoes complex condensation. That the valency of the selenium tends to increase is shown by the formation of crystalline chloro- and bromo-additive products on introducing these halogens into chloroform solutions of the arylselenoglycollic acids. The additive products of bromine are of two types, respectively yellow and red in colour, corresponding to the di- and tetra-bromides. They are easily hydrolysed with the formation of brownish-red oils, a complex change also occurring with the dihalogenides of the arylthioglycollic acids (Pummerer, *Ber.*, 1909, **42**, 2275).

Acidified permanganate solutions are decolorised by the arylselenoglycollic acids, probably with the formation of selenones. With 25% hydrogen peroxide in glacial acetic acid solution, the acids undergo direct oxidation with considerable evolution of heat to furnish well-defined, crystallisable arylselenoxyglycollic acids, $Aryl{\cdot}Se{\cdot}O{\cdot}CH_2{\cdot}CO_2H$ (yields 95%).

Excess of hydrogen peroxide produces no further oxidation, although potassium permanganate is discoloured. This behaviour towards oxidising agents is similar to that of the aryl disulphides and thiodiglycollic acid (Gazdar and Smiles, J., 1908, **93**, 1833; Hinsberg, *Ber.*, 1908, **41**, 2836).

The arylselenoglycollic acids are very resistant to nitric acid and in Carius determinations the temperature must be maintained at 250° for several hours; they develop characteristic colours with concentrated sulphuric acid, the tint varying with the nature of the aryl radical present.

Both the arylseleno- and arylselenoxy-acids form soluble alkali and ammonium salts, the latter being readily dissociated. The alkali salts of the seleno-acids are stable towards alkali fusion at 250°. The silver salts of both series are only very slowly affected by light.

EXPERIMENTAL.

I. *Arylselenoglycollic Acids.*

1. *Phenylselenoglycollic Acid,* $C_6H_5{\cdot}Se{\cdot}CH_2{\cdot}CO_2H$.—Twenty g. of finely powdered selenium were added slowly to magnesium phenyl bromide, from 39 g. of bromobenzene and 6 g. of magnesium in dry ether; brisk effervescence occurred and the mixture was cooled in ice, the reaction being afterwards completed by warming on a water-bath. The cooled mixture was poured on to ice and hydrochloric acid, when a small quantity of hydrogen selenide was evolved and red selenium separated. The ethereal layer was extracted rapidly with 7 g. of caustic potash (100%) in 60 c.c. of water, and to the aqueous solution were added 100 c.c. of alcohol and a solution of sodium chloroacetate (from 6·7 g. of sodium carbonate and 11·8 g. of monochloroacetic acid). Heat was generated and the sodium salt of the glycollic acid was precipitated as a white powder. The reaction was completed on a water-bath, and on concentrating the solution to half its bulk, sodium phenylselenoglycollate crystallised in pinkish-white plates. *Phenylselenoglycollic acid* separated as a pale yellow oil on adding hydrochloric acid to an aqueous solution of its colourless, recrystallised sodium salt. This acid dissolved in a large quantity of boiling water, separating therefrom as a colourless oil, b. p. 160°/750 mm., which became crystalline on standing for several days; m. p. 40°. The potassium salt crystallised in colourless plates with a silvery lustre (Found: C, 44·6; H, 3·7; Se, 36·7. $C_8H_8O_2Se$ requires C, 44·65; H, 3·7; Se, 36·7%).

Phenylselenoglycollic acid, which dissolved in the majority of organic solvents, was only sparingly soluble in cold water; its aqueous solution was acid to litmus. With concentrated sulphuric acid, it developed a deep purple coloration; its bright green copper salt was insoluble in water.

2. p-*Bromophenylselenoglycollic Acid,* $C_6H_4Br{\cdot}Se{\cdot}CH_2{\cdot}CO_2H$.—The condensation of 13·3 g. of selenium and the Grignard reagent from 40 g. of *p*-dibromobenzene and 4 g. of magnesium powder in dry ether was completed on a water-bath and the cooled product subsequently decomposed with ice and hydrochloric acid. The resulting *p*-bromophenylselenomercaptan was extracted with 5 g. of caustic potash and 50 c.c. of water, and to the alkaline solution 80 c.c. of alcohol and an aqueous solution of sodium chloroacetate from 8 g. of monochloroacetic acid were added. After warming on the water-bath for 30 minutes, the solution, on cooling, deposited sodium *p*-bromophenylselenoglycollate slightly pink in colour. The free *acid* crystallised from hot water in colourless, lustrous needles, m. p. 127° (Found: C, 32·7; H, 2·4; Se, 26·9; Br, 27·2.

$C_8H_7O_2BrSe$ requires C, 32·2; H, 2·3; Se, 26·9; Br, 27·2%). *p*-Bromophenylselenoglycollic acid dissolved readily in most organic solvents, but was only sparingly soluble in cold water to a solution having an acid reaction to litmus. The silver salt was only slowly decomposed by light; the green copper salt was insoluble. A deep brown colour was developed in concentrated sulphuric acid.

3. p-*Tolylselenoglycollic acid*, $CH_3{\cdot}C_6H_4{\cdot}Se{\cdot}CH_2{\cdot}CO_2H$, prepared by the general method from magnesium *p*-tolyl bromide, separated from acidified solutions of its recrystallised sodium salt. When crystallised from hot water, this acid was obtained in well-defined, lustrous, acicular prisms melting at 98° and giving a carmine-red coloration with concentrated sulphuric acid (Found: C, 47·1; H, 4·4; Se, 34·4. $C_9H_{10}O_2Se$ requires C, 47·2; H, 4·4; Se, 34·5%).

The alkali and ammonium salts were colourless, crystalline substances soluble in water; the green copper salt was insoluble.

4. *α-Naphthylselenoglycollic acid*, $C_{10}H_7{\cdot}Se{\cdot}CH_2{\cdot}CO_2H$, prepared by the general method from magnesium α-naphthyl bromide, separated from acidified solutions of its sodium salt, and as an oil from hot water. On remaining in a vacuum desiccator for 3 weeks the oil crystallised to a product, m. p. 54°, which gave a green coloration in concentrated sulphuric acid (Found: C, 54·3; H, 3·7; Se, 29·7. $C_{12}H_{10}O_2Se$ requires C, 54·3; H, 3·8; Se, 29·8%).

II. *Arylselenoxyglycollic Acids.*

1. p-*Bromophenylselenoxyglycollic acid*, $C_6H_4Br{\cdot}SeO{\cdot}CH_2{\cdot}CO_2H$, separated in well-defined, colourless needles, m. p. 187°, when 6 c.c. of hydrogen peroxide (25%) were added to 2·9 g. of *p*-bromophenylselenoglycollic acid dissolved in glacial acetic acid, the solution being cooled to moderate the reaction (Found: C, 40·0; H, 2·2; Se, 25·5. $C_8H_7O_3BrSe$ requires C, 40·0; H, 2·25; Se, 25·5%).

p-Bromophenylselenoxyglycollic acid, which dissolved in chloroform or alcohol, was less soluble in ether than the selenoglycollic acid. It dissolved only very slightly in cold, but more so in hot water. The alkali and ammonium salts were colourless and soluble. The pale blue copper salt was insoluble.

2. p-*Tolylselenoxyglycollic acid*, $C_6H_4Me{\cdot}SeO{\cdot}CH_2{\cdot}CO_2H$, produced as in the preceding preparation, separated from glacial acetic acid in colourless crystals, m. p. 165° (Found: C, 44·0; H, 4·0; Se, 32·2. $C_9H_{10}O_3Se$ requires C, 44·1; H, 4·1; Se, 32·2%).

Aqueous or acetic acid solutions of the foregoing arylselenoxy-acids liberated iodine from aqueous potassium iodide.

III. *Halogenides of Arylselenoglycollic Acids.*

1. p-*Tolylselenoglycollic Acid Dibromide*, $C_6H_4Me{\cdot}SeBr_2{\cdot}CH_2{\cdot}CO_2H$.—A solution of 2·29 g. of *p*-tolylselenoglycollic acid (m. p. 98°) in 25 c.c. of dry chloroform was treated with 1·6 g. (1 mol.) of bromine and left in a vacuum desiccator. The dibromide separated in clusters of golden-yellow needles, which decomposed between 90° and 100° with evolution of bromine (Found: Br, 40·9; Se, 20·3. $C_9H_{10}O_2Br_2Se$ requires Br, 41·1; Se, 20·3%).

An aqueous solution of potassium iodide reacted with the dibromide, liberating iodine and regenerating a quantity of the original acid together with a proportion of the corresponding selenoxy-acid. The dibromide was unstable in moist air and was easily hydrolysed, giving brownish-red oils of complex constitution.

2. p-*Tolylselenoglycollic acid tetrabromide*,

$$C_6H_4Me{\cdot}SeBr_4{\cdot}CH_2{\cdot}CO_2H,$$

prepared in a similar manner to that described above by the addition of 3·8 g. of bromine (20% in excess of 2 mols.) to 2·29 g. of *p*-tolylselenoglycollic acid dissolved in dry chloroform, separated in small, scarlet needles which readily decomposed on warming (Found: Br, 58·3; Se, 14·4. $C_9H_{10}O_2Br_4Se$ requires Br, 58·3; Se, 14·4%).

The tetrabromide was readily hydrolysed and liberated iodine from an aqueous solution of the acid.

3. p-*Bromophenylselenoglycollic acid dibromide*,

$$C_6H_4Br{\cdot}SeBr_2{\cdot}CH_2{\cdot}CO_2H,$$

prepared as above from 2·94 g. of *p*-bromophenylselenoglycollic acid and 1·6 g. of bromine, formed golden-yellow crystals decomposing at 120—130° with evolution of bromine (Found: Br, 52·8; Se, 17·4. $C_8H_7O_2Br_3Se$ requires Br, 52·9; Se, 17·4%).

4. p-*Bromophenylselenoglycollic acid tetrabromide*,

$$C_6H_4Br{\cdot}SeBr_4{\cdot}CH_2{\cdot}CO_2H,$$

prepared from 2·94 g. of *p*-bromophenylselenoglycollic acid and 3·8 g. of bromine in dry chloroform, formed scarlet needles which decomposed on warming with evolution of bromine (Found: Br, 65·0; Se, 12·8. $C_8H_7O_2Br_5Se$ requires Br, 65·15; Se, 12·9%).

The authors desire to express their thanks to the Government Grant Committee of the Royal Society and to the University of Birmingham Research Committee for grants which have helped to defray the expense of this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

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CCXXXIV.—*Aromatic Derivatives of Germanium.*

By GILBERT T. MORGAN and HARRY DUGALD KEITH DREW.

WHEN germanium tetrabromide is treated with a large excess of magnesium phenyl bromide (36 mols.) it yields *germanium tetraphenyl* or *tetraphenylgermane*, $Ge(C_6H_5)_4$, *triphenylgermanium bromide*, $Ge(C_6H_5)_3Br$, and the less phenylated germanium bromides, $Ge(C_6H_5)_2Br_2$ and $Ge(C_6H_5)Br_3$. The first two products are readily separated, but the latter pair, which do not solidify when mixed, have been identified by the isolation of their hydrolytic products.

Hexaphenyldigermane, $(C_6H_5)_3Ge{\cdot}Ge(C_6H_5)_3$, has not been detected among the products of the Grignard reaction, so that under these experimental conditions there is little or no tendency for junction of two atoms of the metal (compare with tin and lead), but the compound is readily prepared by the action of sodium on the triphenylgermanium bromide.

$$2GePh_3Br + 2Na = Ph_3Ge{\cdot}GePh_3 + 2NaBr.$$

The production of tetraphenylgermane and hexaphenyldigermane completes the following series :—

	CPh_4.	$SiPh_4$.	$GePh_4$.	$SnPh_4$.	$PbPh_4$.
M. p.	272°	233°	230—231°	225—226°	224—225°
	C_2Ph_6.	Si_2Ph_6.	Ge_2Ph_6.	Sn_2Ph_6.	Pb_2Ph_6.
M. p.	145—147°*	354°	340°	237°	155°*

* These abnormally low melting points are due to dissociation.

Hexaphenyldigermane when examined in dilute benzene solutions shows no recognisable tendency to dissociation.

On hydrolysis the solid triphenylgermanium bromide yielded *triphenylgermanium oxide*, $(C_6H_5)_3Ge{\cdot}O{\cdot}Ge(C_6H_5)_3$, corresponding with the silicon compound, $Ph_3Si{\cdot}O{\cdot}SiPh_3$. The analogue, $Ph_3Ge{\cdot}OH$, of triphenylsilicon hydroxide was not isolated.

Hydrolytic Products from Diphenylgermanium Dibromide and Phenylgermanium Tribromide.—When only 5 molecular proportions of magnesium phenyl bromide are employed to one of germanium tetrabromide, there is no formation of tetraphenylgermane but the product contains a mixture of mono-, di-, and tri-phenylgermanium bromides.

Diphenylgermanium dibromide yielded on hydrolysis two well-defined complex substances derived by dehydration from the hypothetical dihydroxide or diol, $(C_6H_5)_2Ge(OH)_2$. These products,

which have considerable capacity for crystallisation, are *trianhydrotetrakisdiphenylgermanediol*,

$$HO{\cdot}GePh_2{\cdot}O{\cdot}GePh_2{\cdot}O{\cdot}GePh_2{\cdot}O{\cdot}GePh_2{\cdot}OH$$

(I), m. p. 149°, and *tetra-anhydrotetrakisdiphenylgermanediol*,

$$O\langle\begin{matrix}GePh_2{\cdot}O{\cdot}GePh_2\\GePh_2{\cdot}O{\cdot}GePh_2\end{matrix}\rangle O$$

(II), m. p. 218°.

The formation of these complicated anhydro-compounds recalls the results obtained by Kipping and his collaborators (J., 1912, **101**, 2108, 2125; 1914, **105**, 484) on hydrolysing diphenylsilicon dichloride, when the diol $Ph_2Si(OH)_2$ and four anhydrides were identified. The two silicon derivatives corresponding with formulæ I and II melt respectively at 128—129° and 200—201°. Diphenylgermanium dibromide also undergoes hydrolysis to an insoluble amorphous substance (p. 1765), from which it is regenerated by concentrated hydrobromic acid.

Owing to this tendency to form anhydrides it is obvious that hydrolysis of a mixture of diphenylgermanium dibromide and phenylgermanium tribromide might lead to an anhydro-diol derived from more than one of the reacting bromides. This anticipation was realised by the isolation of a substance (m. p. 275°) having a composition and molecular weight approximating to $Ge_5(C_6H_5)_8O_6$, which may be regarded as a combination of $3GePh_2O$ with $GePhO{\cdot}O{\cdot}GePhO$, these oxides being derived from the hydrolysis of diphenylgermanium dibromide and phenylgermanium tribromide, respectively. This product, which arises apparently from a chance condensation of the two different oxy-compounds, was only obtained in one experiment.

The hydrolysis of phenylgermanium tribromide leads to *phenylgermanonic* or *germanibenzoic acid*, a colourless uncrystallised product soluble in aqueous caustic alkalis. Its properties in regard to degree of hydration vary with the experimental conditions of its preparation and isolation. In all probability its composition varies within the limits $C_6H_5{\cdot}GeO{\cdot}OH$ and $C_6H_5{\cdot}GeO{\cdot}O{\cdot}OGe{\cdot}C_6H_5$ (III) and the analytical numbers approximate to an intermediate complex formula still containing hydroxyl groups. Phenylgermanonic acid or germanibenzoic acid therefore comes into line with silicobenzoic acid and its analogues, which have been shown conclusively by Kipping and his collaborators (J., 1914, **105**, 679; 1915, **107**, 459) to consist of mixtures of condensation products varying in composition with the conditions of hydrolysis of the halogenated silicanes.

The foregoing results obtained with oxygenated phenylgermanium compounds indicate that the reactions of these substances are similar

to those of the oxyarylsilicon derivatives but of a somewhat simpler type with less tendency to the formation of syrups, colloids and infusible mixtures. In this respect germanium forms a link between silicon and tin, and the germanium atom should exhibit a tetrahedral distribution of valencies.

EXPERIMENTAL.

I. *Interaction of Germanium Tetrabromide with a Large Excess of Magnesium Phenyl Bromide.*

1. The Grignard reagent from 5·7 g. of magnesium, 30·2 g. of bromobenzene, and 120 c.c. of ether (36 mols. PhMgBr) was added to 2·1 g. of germanium tetrabromide in 75 c.c. of ether, and the mixture heated for 2 hours. The dark orange-yellow liquid was poured on to ice and acidified with hydrobromic acid, when a creamy white powder remained consisting of *tetraphenylgermane* (0·8 g. or 40%). The ethereal filtrate and extracts, dried over sodium sulphate and concentrated, yielded 0·5 g. of *triphenylgermanium bromide;* the final mother-liquor containing the less phenylated products was worked up as described on p. 1765.

2. During the action of less Grignard reagent (8 mols. PhMgBr) on 4·4 g. of germanium tetrabromide in 25 c.c. of pure chloroform (Boots') heat was generated. The resulting liquid, after being warmed on the water-bath for 1½ hours, was treated as above and yielded 0·93 g. of tetraphenylgermane (22%) and 1·1 g. of triphenylgermanium bromide (26%), the separation of the latter being hastened by adding petroleum (b. p. 60—80°). The ether-petroleum mother-liquors, distilled in steam to remove diphenyl, left a semi-solid yellowish-brown mass which after trituration left 0·4 g. of colourless crystalline *triphenylgermanium oxide*. The oily bromides were worked up as on p. 1765, whereas the aqueous layer from the hydrolysis of the Grignard product by ice deposited gradually a small amount of *phenylgermanonic* or *germanibenzoic acid*.

Tetraphenylgermane (*Germanium tetraphenyl*), $GePh_4$, crystallised from petroleum (b. p. 60—80°) in lustrous, refractive, transparent, prismatic needles, colourless in small quantities, creamy white in bulk. Very stable on heating, it melted at 230—231° and could be volatilised without decomposition (Found: C, 75·4; H, 5·6; Ge, 18·5. $C_{24}H_{20}Ge$ requires C, 75·7; H, 5·3; Ge, 19·0%).

Tetraphenylgermane was insoluble in water, sparingly soluble in ether, light petroleum, or cold acetone, and dissolved more readily in benzene, separating therefrom in acicular prisms. Boiling aqueous caustic alkalis had no effect on this substance; it was insoluble in cold concentrated sulphuric acid, but on warming sulphonation occurred destructively with elimination of phenyl

groups. Fuming nitric acid or a mixture of nitric and sulphuric acids caused nitration and oxidation with evolution of nitrous fumes.

Triphenylgermanium bromide, $GePh_3Br$, formed large, colourless, transparent, six-sided, refractive, prismatic needles or small, compact prisms. Insoluble in water but somewhat readily soluble in ordinary organic media, it was best crystallised from petroleum (b. p. 40—80°); it melted at 138° to a colourless liquid (Found: C, 56·6; H, 4·1; Br, 20·7. $C_{18}H_{15}BrGe$ requires C, 56·3; H, 3·9; Br, 20·8%).

Triphenylgermanium bromide became hydrolysed superficially to its oxide by boiling water or by warm aqueous caustic alkalis. It arose as a by-product in the preceding preparations, but became the chief product when five molecular proportions of the Grignard reagent were employed to one of germanium tetrabromide. When 9·3 g. of the latter substance were used, the ethereal solution, after heating on the water-bath and subsequent treatment with ice and hydrobromic acid, yielded, on concentration of the ether layer, 2·5 g. (or 27%) of triphenylgermanium bromide. The residual oil was then treated with aquo-alcoholic silver nitrate, filtered from silver bromide, and the filtrate evaporated and distilled in steam, when diphenyl and *o*-nitrophenol were removed in the distillate. The non-volatile semisolid residue was fractionated from boiling petroleum (b. p. 60—80°) and from cold ether, when the following crystalline substances were separated: (i) a colourless compound (0·7 g.) melting at 275°, practically insoluble in cold ether or light petroleum and only sparingly soluble in the latter on warming (see pp. 1761, 1767); (ii) *tetra-anhydrotetrakisdiphenylgermanediol* (0·2 g.) melting at 218°, more soluble in ether or petroleum (see pp. 1761, 1766); (iii) an orange-yellow substance (0·1 g.) melting from 106° to 112°, very soluble in organic solvents or in water. This product (C, 51·3; H, 4·5%) contained no germanium and did not depress the melting point of ordinary *p*-nitrophenol (C, 51·8; H, 3·6%), but unlike the latter it was intensely yellow and more soluble in cold water. Being formed from phenylated germanium derivatives and silver nitrate in the absence of mineral acids, it may consist in part of an *aci*-form of *p*-nitrophenol. In addition to these solid products there was a considerable proportion of uncrystallisable germaniferous material which was worked up subsequently as described on p. 1766.

Triphenylgermanium Oxide, $Ph_3Ge{\cdot}O{\cdot}GePh_3$.—An alcoholic solution of triphenylgermanium bromide was boiled with silver nitrate, filtered from silver bromide, and diluted with water, when the oxide was obtained in quantitative yield. This product crystallised from hot petroleum (b. p. 60—80°) in transparent, colourless

prisms melting to a colourless liquid at 182—183°; it separated from ethyl acetate in thin, six-sided plates (Found: C, 69·2; H, 4·9; Ge, 23·2. $C_{36}H_{30}OGe_2$ requires C, 69·35; H, 4·85; Ge, 23·2%).

In organic media triphenylgermanium oxide was more soluble than tetraphenylgermane but less so than triphenylgermanium bromide; it was unattacked by 50% aqueous caustic potash, but was reconverted quantitatively into triphenylgermanium bromide by hydrobromic acid (*d* 1·45).

Hexaphenyldigermane, $Ph_3Ge{\cdot}GePh_3$. — Triphenylgermanium bromide (3 g.) dissolved in 37 c.c. of dry xylene was heated for 3 hours with excess of "molecular" sodium. The filtered solution deposited on cooling 2·2 g. of hexaphenyldigermane, and a further amount was obtained on concentration. The final filtrate contained a small quantity of the more soluble triphenylgermanium oxide arising as a by-product.

Hexaphenyldigermane separated from hot benzene in large, colourless, transparent cubes crumbling into powder on exposure to air: loss of benzene at 100° = 24·3%, corresponding with 3 mols. of C_6H_6. It was sparingly soluble in cold but more soluble in hot chloroform, separating therefrom in colourless micro-crystals, m. p. 340° [Found: C, 70·8, 70·7; H, 5·1, 5·3; Ge, 23·5; *M*, ebullioscopic in benzene, 566 ($c = 0·595$), 560 ($c = 1·328$). $C_{36}H_{30}Ge_2$ requires C, 71·2; H, 5·0; Ge, 23·85%; *M*, 606·8].

Hexaphenyldigermane was insoluble in boiling aqueous caustic soda, but on boiling with alcoholic silver nitrate a slight blackening occurred owing to liberation of silver.

Phenylgermanonic Acid (*Germanibenzoic Acid*, p. 1761).—The aqueous mother-liquors from the hydrolysis of the Grignard mixture slowly deposited a white, colloidal precipitate, which was purified for analysis by redissolving in aqueous caustic soda, the filtered solution being then acidified, when the white, amorphous powder separated and was dried at 100° (Found: C, 39·9; H, 3·2. The simplest formula, $C_6H_6O_2Ge$, requires C, 39·5; H, 3·3%).

From concentrated solutions of its sodium salt, phenylgermanonic acid separated at once (hydrogel form), but in dilute solutions it remained dissolved (hydrosol condition) and separated only after several weeks.

II. *Interaction of Germanium Tetrabromide and Magnesium Phenyl Bromide* (5 *mols.*).

A Grignard solution, prepared from 48·4 g. of bromobenzene (5 mols.), 9·1 g. of magnesium, and 200 c.c. of ether, was added slowly to an ice-cold solution of 24·5 g. (1 mol.) of germanium tetrabromide in 100 c.c. of ether, moisture and carbon dioxide being

excluded. The heavy colourless oil which separated persisted after heating on the water-bath. The cooled mixture was decomposed by ice and 50 c.c. of hydrobromic acid (*d* 1·45), when the crackling sound produced by the hydrolysis of germanium tetrabromide showed that this substance was not completely attacked even by excess of Grignard reagent. The solution was extracted with ether and the mixed ethereal extracts were dried over sodium sulphate. The aqueous layer, which gave no precipitate of phenylgermanonic acid (germanibenzoic acid) either when left or when partially neutralised, contained no other organic derivatives of germanium.

The ethereal extract, concentrated to a small bulk, gave 9 g. (37·5%) of *triphenylgermanium bromide*.

The residual oil, which contained a complex mixture of triphenylgermanium bromide, the less phenylated germanium bromides, and chiefly diphenylgermanium dibromide together with diphenyl and traces of bromobenzene, was dissolved in 150 c.c. of alcohol and added to 20 g. of silver nitrate in 100 c.c. of alcohol and 40 c.c. of water, when a dark brown precipitate separated. The mixture was heated under reflux for an hour and the alcoholic filtrates (A) separated from a black precipitate (B). This precipitate B, which consisted mainly of silver bromide but contained some organic germanium compound, was boiled with ammonia (*d* 0·88),* when a black residue remained which was extracted successively with aqueous sodium thiosulphate and dilute nitric acid, leaving 1·5 g. of a white, amorphous organic germanium compound. This substance melted partly at 260° and was insoluble in organic solvents, aqueous alkalis or ammonia; it was converted by hydrobromic acid into an oily bromide, from which the original amorphous substance was recovered by the action of water. This uncrystallisable product was also obtained by the hydrolysis of the oily bromide from tetra-anhydrotetrakisdiphenylgermanediol, m. p. 218°.

The alcoholic filtrate A was evaporated and the oily residue distilled in steam, when diphenyl and *o*-nitrophenol passed over. The residue, a solid of pitchy consistence, was dissolved in ether and the yellow solution filtered and concentrated until an orange-yellow, semi-crystalline mass separated. This product, after extraction with cold petroleum (b. p. 80—100°) to remove diphenyl and other more soluble impurities, furnished 5 g. of an almost

* The ammoniacal filtrate deposited on cooling lustrous spangles of silver bromide having a highly refractive reflex. This product was an insensitive form of the bromide, for it retained its bright metallic lustre after months of exposure to light. The ammoniacal liquor, which contained traces of organic derivatives of germanium, had the property of converting more yellow silver bromide to this insensitive form, the spangles separating at the surface of the solution.

colourless mixture of organic germanium derivatives now free from bromine. Repeated solution of this mixture in ethyl acetate followed by fractional crystallisation and hand-picking of the resulting crystals led to a separation of the following substances :—

1. *Triphenylgermanium oxide*, m. p. 182—183° (see p. 1763), separating from ethyl acetate in thin, rhomboidal or pentagonal plates.

2. *Tetra-anhydrotetrakisdiphenylgermanediol* (Formula II), crystallising in colourless, cubical and prismatic forms, the latter with bevelled and facetted faces. This complex diol was purified by crystallisation from petroleum or ethyl acetate, in which it was readily soluble, and then melted indefinitely at 218° [Found: C, 59·4, 59·1; H, 4·25, 4·4. $(C_{12}H_{10}OGe)_x$ requires C, 59·4; H, 4·2%.

Fig. 1.

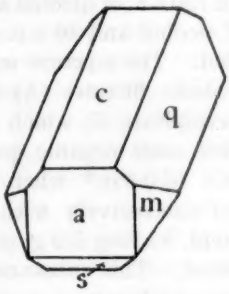
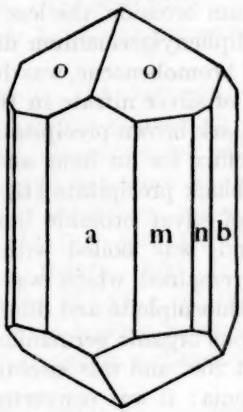


Fig. 2.



Found : by the ebullioscopic method in benzene ($c = 1·48$), M, 905. $(C_{12}H_{10}OGe)_4$ requires M, 970].

3. *Trianhydrotetrakisdiphenylgermanediol* (Formula I), m. p. 149°, obtained in colourless, hexagonal prisms or flattened, rhomboidal crystals with bevelled edges (Found : C, 58·8; H, 4·6. $C_{48}H_{42}O_5Ge_4$ requires C, 58·3; H, 4·25%).

Crystallographic Examination.

Two of the foregoing substances (Nos. 2 and 3) were kindly examined by Dr. T. V. Barker, who reports as follows :—

Tetra-anhydrotetrakisdiphenylgermanediol (Fig. 1).—The crystals of this substance are monoclinic with the forms $m(110)$, $a(100)$, $q(011)$, $c(001)$ and $s(201)$ developed in the proportions given in Fig. 1. The axial ratios, $a : b : c = 1·491 : 1 : 1·018$, $\beta = 111° 42'$, were computed from the following results given by four crystals.

	m.	*a*.	*q*.	*c*.	*s*.
ϕ.....	0° 0′	0° 0′	68° 21′	*68° 18′	*137° 0′
ρ.....	35 45	90 0	*46 35	90 0	90 0

Optically, the crystals are positive; the axial plane is $b(010)$, and one optic axis is nearly normal to $a(100)$.

Trianhydrotetrakisdiphenylgermanediol (Fig. 2).—The crystals are orthorhombic with the forms $a(100)$, $m(110)$, $n(120)$, $b(010)$, and $o(111)$ developed in the proportions given in Fig. 2. The axial ratios, $a : b : c = 0{\cdot}9539 : 1 : 0{\cdot}5399$, were computed from the following measurements derived from four crystals.

	b.	*n*.	*m*.	*a*.	*o*.
ϕ	0° 0′	27° 50′	*46° 21′	90° 0′	46° 21′
ρ	90 0	90 0	90 0	90 0	*38 2

Optically, the positive acute bisectrix is parallel to the *c*-axis, and the axial plane is *a*.

The Complex Diol melting at 275°.—When recrystallised from ethyl acetate, it separated in large, transparent, colourless prisms melting at 231° and containing solvent of crystallisation. At 140° the loss of weight was 4·45%, corresponding approximately with 2 mols. of diol combined with one of ethyl acetate (theory 3·9%). Crystallised from carbon tetrachloride, the compound melted to a transparent, colourless liquid at 277—278° but rather indefinitely [Found : C, 53·8; H, 3·9; Ge, 33·6; *M*, ebullioscopic in benzene ($c = 1{\cdot}000$), 1003. $C_{48}H_{40}O_6Ge_5$ requires C, 53·6; H, 3·7; Ge, 33·7%; *M*, 1074].

This complex diol was insoluble in water, dilute alcohol, ether, or petroleum and only sparingly soluble in other organic media.

Note on the Analysis of Aromatic Germanium Compounds.

In estimating carbon and hydrogen the combustion was effected entirely with oxygen in a tube containing copper oxide and lead chromate. The oxygenated germanium compounds required very prolonged heating at high temperatures in order to oxidise the last traces of carbon, which otherwise remained in the boat or on the side of the tube as a refractory black material.

For the estimation of germanium the weighed substance was digested during 8 or 10 hours with 18 c.c. of concentrated sulphuric acid (A.R. quality) in a flask with a ground-in air-condenser. The cooled liquid and undissolved germania were washed into a conical flask with 150 c.c. of water, any adherent germania being removed by boiling aqueous sodium carbonate (A.R.). The clear solution was thoroughly saturated with washed hydrogen sulphide and left in the closed flask for a day. The pinkish-white sulphide containing free sulphur and some organic matter was collected on a Gooch crucible with ashless paper filter, and washed successively with 4*N*-sulphuric acid saturated with hydrogen sulphide and aqueous hydrogen sulphide. After drying at 100° the precipitate and the portion

remaining on the filter-paper were converted into germania in separate porcelain crucibles by treatment with dilute and then with concentrated nitric acid. On igniting the crucibles strongly, germania was obtained in a perfectly white condition.

The authors desire to express their thanks to Messrs. Brunner Mond and Company, Limited, for a grant which has partly defrayed the expense of this investigation.

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CCXXXV.—*The Stability of Additive Compounds between Esters and Acids.*

By JAMES KENDALL and JAMES ELIOT BOOGE.

THE parallelism between the electrical conductivity of an acid solution and its catalytic activity in ester hydrolysis formed one of the strongest supports of the Arrhenius ionisation theory in its early stages. More accurate measurements made it evident, however, that direct proportionality between hydrogen-ion concentration and reaction velocity could not be claimed. Other divergences were soon noted; not only did the rate of hydrolysis increase more rapidly than hydrogen-ion concentration, it also increased with the ester concentration. Many investigations have been performed upon ester–acid–water systems to explain these divergences, and several interesting theories—for example, the theory of the catalytic activity of the undissociated molecule and the theory of the anticatalytic effect of water—have been developed. The radiation hypothesis also has been applied to the problem by Lewis and his co-workers, but the mechanism of acid catalysis of ester hydrolysis is still unsolved.

Some advance has been made, nevertheless, in the general recognition of the fact that the concentrations of the reacting molecular species in a solution of this complicated character cannot be directly calculated from its composition. Formation of additive compounds certainly disturbs the stoicheiometric ratios very materially, and inasmuch as it appears most probable that the hydrolysis is effected in steps, with these compounds as intermediate products, it is clearly important to examine their character and stability as thoroughly as possible.

The first direct evidence of the existence of additive compounds between esters and acids was furnished by the present authors in an earlier article (*J. Amer. Chem. Soc.*, 1916, **38**, 1712), in which

extensive references to previous work will also be found. Thirteen definite compounds of the general type R·CO·OR′,HX were isolated, and it was shown qualitatively that the stability of such compounds in the liquid state increased as the radicals R and R′ were made more electropositive, or as the radical X was made more electronegative. The most stable compounds were consequently obtained when an *ester of a weak acid* (*e.g.*, ethyl acetate) was paired with a *strong acid* (*e.g.*, trichloroacetic acid), but some compound formation was still indicated even in such an unfavourable system as methyl oxalate–acetic acid.

From the results of this investigation, the general conclusion was drawn that the formation of an ester–acid additive compound constitutes the first step in ester hydrolysis. The following articles discuss the stability of these complexes quantitatively, and also examine the evidence with regard to their dissociation and the formation of additive compounds of other types in the presence of the third component—water.

The progressive dissociation of ester–acid compounds on addition of water may be postulated as due to three distinct causes. In the first place, the effect may be purely *diluent*, the equilibrium point in the reaction $R{\cdot}CO{\cdot}OR',HX \rightleftharpoons R{\cdot}CO{\cdot}OR' + HX$ being shifted in the forward direction merely by the diminution in the concentrations of ester and acid as we proceed from the anhydrous system to a dilute aqueous solution. Secondly, the water may disturb the equilibrium still further by combining with the free acid or ester to form binary complexes of the type HX,H_2O or $R{\cdot}CO{\cdot}OR',H_2O$. Thirdly, the water may combine with the ester–acid compound to give a ternary complex of the type $R{\cdot}CO{\cdot}OR',HX,H_2O$.

In order to separate these three factors, as far as is feasible, the problem has been taken up in stages. First, the extent of the dissociation of certain typical ester–acid compounds into their components on fusion has been examined by comparing the freezing-point depressions induced by addition of free ester, an inert solute (benzene), and the active solute water. Next, the extent to which ester–acid compounds are still existent in a dilute solution, when the solvent is inert, has been investigated by determining the freezing-point depression curves of benzene on addition of ester and of acid, separately and in company. Binary systems of the types acid–water and ester–water are then discussed, and the final and most intricate case of all (the ternary system: ester–acid–water) is thus approached only after the results of the preceding work have furnished useful information as to the most promising methods of attack.

The Stability of Ester–Acid Compounds on Fusion.

Three compounds are examined in this section, the complexes chosen being those formed by trichloroacetic acid with ethyl acetate, benzyl benzoate and methyl succinate respectively. The extent of dissociation in each case is calculated from the form of the freezing-point depression curves of the compound, as indicated in Fig. 1.

This method was first suggested by Bancroft (*J. Physical Chem.*, 1899, **3**, 72) and developed in detail by Kremann (*Monatsh.*, 1904, **25**, 1215). Unfortunately, the equations arrived at by Kremann are not free from error (Roozeboom and Aten, *Z. physikal. Chem.*, 1905, **53**, 449) and it is important to note that the method is *strictly* applicable only when the heat of dissociation of the complex is zero. Nevertheless, since in mixtures of organic substances heats of dissociation are in general but small, and the stability of a given compound may be regarded as constant over a restricted temperature range, the method may be utilised to give approximately accurate values, the procedure being briefly as follows:

If an additive compound is perfectly stable on fusion, its freezing-point curve on addition of y moles of either component to 100 moles of compound will be given by the equation:

$$-\log_e\left(\frac{100}{100+y}\right)=\frac{Q}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right) \quad . \quad . \quad . \quad \text{(I)}$$

where Q is the molar heat of fusion of the compound in calories, T_0 its absolute temperature of fusion in the pure state, T its absolute temperature of fusion in the solution, and R the gas constant, 1·988. If, on the other hand, the percentage dissociation of the pure compound on fusion is x, then addition of y moles of either component to 100 moles of the compound will repress this dissociation to a smaller value x', and we obtain the equation:

$$-\log_e\left(\frac{100-x'}{100+x'+y}\right)=\frac{Q}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right) \quad . \quad . \quad \text{(II)}$$

the graph for which will vary more and more from that given by equation (I), according as x increases. Various trial values may be assumed for x, and the resultant curves compared with that obtained experimentally until accordance is reached.

It remains to show how the "unknowns" in equation (II) may be evaluated. If K is the dissociation constant of the reaction $R{\cdot}CO_2R'$, $HX \rightleftharpoons R{\cdot}CO_2R' + HX$, then we have the two equations:

$$\left(\frac{x}{100+x}\right)^2=K\left(\frac{100-x}{100+x}\right) \quad . \quad . \quad . \quad \text{(III)}$$

and

$$\frac{x'(x'+y)}{(100+x'+y)^2}=K\left(\frac{100-x'}{100+x'+y}\right) \quad . \quad . \quad \text{(IV)}$$

whence, as K is known for each assumed value of x, the variation of x' with y is derived. Q must be determined either calorimetrically, or (by calculation) from the form of the freezing-point curve when an inert solute is added. R, of course, is known. The only remaining factor, T_0 (the hypothetical freezing point for the pure compound in the absence of dissociation products), is obtained from equation (II) by putting $y = 0$, when x' becomes x and T becomes the experimental freezing point.

1. *The Compound Ethyl Acetate–Trichloroacetic Acid.*—This compound, as obtained by mixing equimolecular quantities of its carefully purified components, melted sharply at $-26{\cdot}8°$. A simplified Beckmann type of apparatus was used to determine the freezing-point depression curves of this material on addition of ethyl acetate, benzene and water, and in view of the approximate nature of the method and the difficulty of working at low temperatures and maintaining anhydrous conditions, no attempt was made to obtain readings for the freezing-point depression (ΔT) to a greater accuracy than $0{\cdot}05°$ in the more dilute, or $0{\cdot}1°$ in the more concentrated solutions. Additions of solute were made by means of a Grethan pipette. Compositions are expressed throughout in molecular percentages.

TABLE I.

Freezing-point Depression Curves of the Compound: Ethyl Acetate–Trichloroacetic Acid.

Solutes.						
Ethyl acetate	Mol. %	4·23	9·55	15·45	22·75	34·5
	$\Delta T°$	0·15	0·60	1·30	2·6	5·5
Benzene	Mol. %	3·27	7·74	13·4	21·3	23·2
	$\Delta T°$	0·80	2·0	3·2	5·3	6·0
Water	Mol. %	7·47	15·24	21·3	33·7	
	$\Delta T°$	1·90	3·9	5·5	9·6	

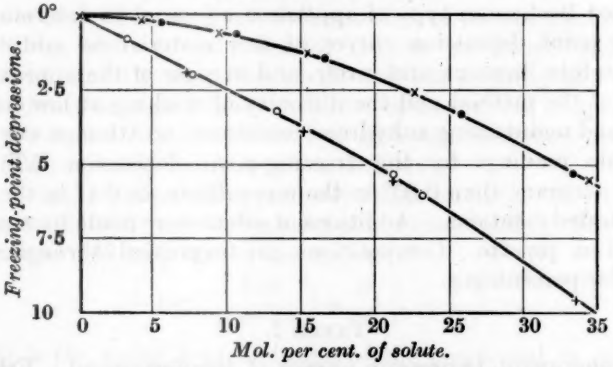
These results are expressed graphically in Fig. 1. Partial dissociation of the compound on fusion is shown by the fact that ethyl acetate does not give the same freezing-point depression curve as the other solutes. By application of equation (II) above, it is found that the approximate degree of dissociation of the compound in the liquid state is 12%. The assumption of this value for x gives practically perfect agreement throughout the whole length of the experimental and calculated curves.

The value for Q, obtained calorimetrically for use in these calculations, was 5170 ± 50 calories. This was checked by a rather intricate calculation from the freezing-point depression curve obtained with benzene as solute. The value so derived was 5150 ± 100 calories.

A most unexpected result in the above table is the identity of the freezing-point depression curves obtained with benzene (an inert solute) and water (presumably reactive). In this connexion it may be mentioned that the points on the water curve did not change significantly with time during the course of the determinations, hydrolysis effects evidently being quite slow at the low temperatures involved. Comment upon the abnormal position of the water curve will be made at the conclusion of this article.

FIG. 1.

Freezing-point depression curve of the compound: ethyl acetate–trichloroacetic acid.



○ = *Benzene.* + = *Water.* × = ***Ethyl acetate (experimental).*** ● = *Ethyl acetate (calculated for 12% dissociation of pure compound on fusion).*

2. *The Compound Benzyl Benzoate–Trichloroacetic Acid.*—The pure compound in this case melted sharply at 13·6°. The freezing-point depression results obtained with benzyl benzoate, benzene, and water as solutes are given below.

TABLE II.

Freezing-point Depression Curves of the Compound: Benzyl Benzoate–Trichloroacetic Acid.

Solutes.						
Benzyl benzoate	Mol. %	4·54	9·92	15·75	26·1	51·7
	$\Delta T°$	0·10	0·35	0·80	2·0	8·5
Benzene	Mol. %	5·37	13·6	27·6	42·6	
	$\Delta T°$	1·40	3·6	8·1	14·4	
Water	Mol. %	7·58	10·87	19·7	27·0	
	$\Delta T°$	1·80	2·9	5·8	8·6	

Again the benzene and water curves are very nearly identical. Calculation of the degree of dissociation of the compound on fusion from the position of the benzyl benzoate curve, using a calorimetrically determined value for Q of 5660 $\pm$ 40 calories, leads to a value of (approximately) 35%.

3. *The Compound Methyl Succinate–Trichloroacetic Acid.*—A pure sample of this compound (which contains one molecule of ester to two of acid) melted sharply at 8·3°.

TABLE III.

Freezing-point Depression Curves of the Compound: Methyl Succinate–Trichloroacetic Acid.

Solutes.						
Methyl succinate	Mol. %	4·52	9·27	18·55	29·3	44·8
	$\Delta T°$	0·30	0·50	1·70	3·8	9·6
Benzene	Mol. %	5·55	11·97	21·8	31·3	
	$\Delta T°$	0·85	1·90	4·0	6·3	

The calculation of the degree of dissociation of this 1 : 2 compound from the position of the methyl succinate curve is more complicated than in the previous cases. It is also more uncertain, since a compound of the type AB_2 may give an intermediate dissociation product AB as well as its simple components A and B. Fortunately, this particular compound is exceptionally stable, so that it is still possible to fix its degree of dissociation between the upper and lower limits of 6 and 4% respectively. In this calculation, the value used for Q (9600 calories) is derived from the benzene curve, assuming this for the sake of simplicity to be ideal.

The Stability of Acid–Ester Compounds in Dilute Benzene Solution.

The next step in the investigation was to determine the stability of acid–ester compounds in the presence of a large excess of an inert solvent—benzene.

The compound ethyl acetate–trichloroacetic acid was first studied. Table IV gives the freezing-point depression curves of benzene with ester, acid and compound as solutes. The same data are represented graphically in Fig. 2. For comparison, the ideal curve [obtained by substituting $Q = 2370$ calories and $T_0 = 278{\cdot}48$ in the equation $-\log_e(1-x) = Q/R \,.\, (1/T - 1/T_0)$, where x = mol. % of solute] is also added.

TABLE IV.

Freezing-point Depression Curves of Benzene (System: Ethyl Acetate–Trichloroacetic Acid).

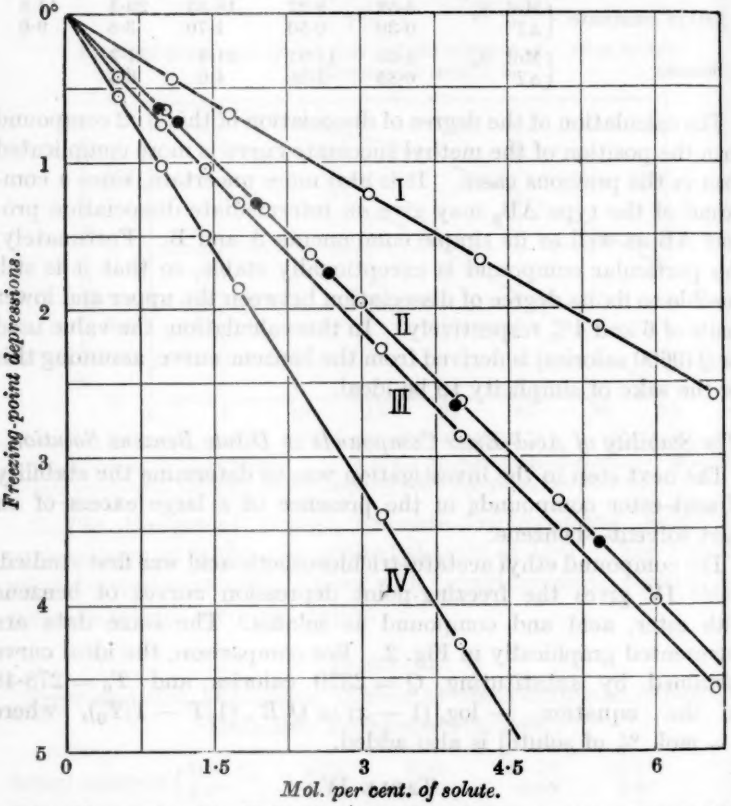
Solutes.								
Ideal	Mol. %	1·0	2·0	2·5	3·0	4·0	5·0	6·0
	$\Delta T°$	0·652	1·308	1·637	1·967	2·631	3·299	3·967
Ethyl acetate	Mol. %	0·965	1·138	1·934	2·670	3·966	5·425	
	$\Delta T°$	0·643	0·727	1·276	1·775	2·640	3·598	
Trichloro-acetic acid	Mol. %	0·543	1·063	1·654	3·068	4·22	5·41	6·63
	$\Delta T°$	0·213	0·432	0·672	1·222	1·674	2·120	2·582
Acid–ester compound	Mol. %	0·520	0·952	1·410	1·743	3·205	4·065	5·075	6·62
	$\Delta T°$	0·417	0·740	1·038	1·273	2·264	2·866	3·532	4·580

Specially purified benzene was employed in this work, and temperatures were read to 0·001° by the Beckmann method. The thermometer employed was calibrated by the Bureau of Standards, and all precautions were taken to ensure accuracy.

The ethyl acetate curve, it will be seen from the diagram, follows

FIG. 2.

System: ethyl acetate–trichloroacetic acid. Benzene as solvent.



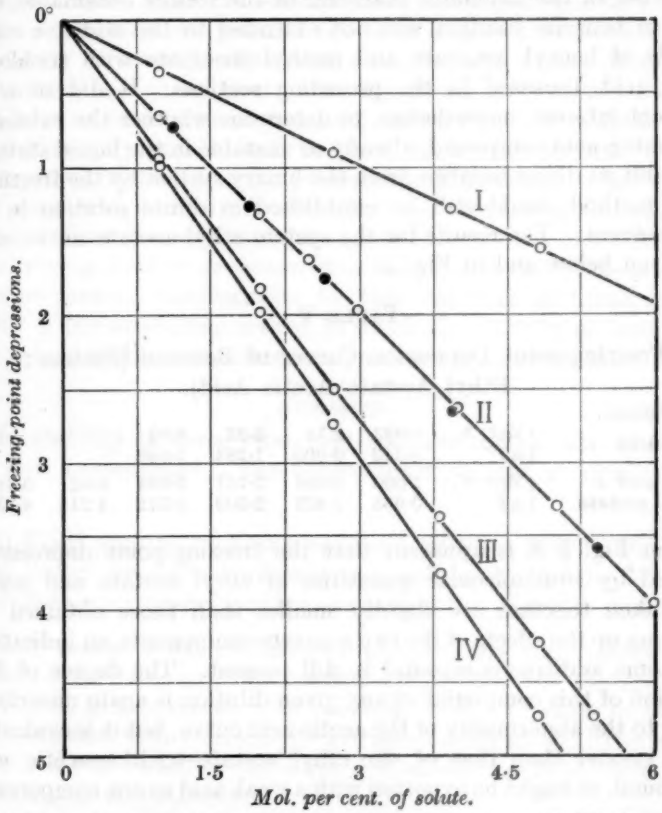
I *Trichloroacetic acid.* II *Ethyl acetate* (●); *ideal curve* (○). III *Additive compound.* IV *Sum of* I *and* II.

the ideal within error limits. The freezing-point depressions induced by trichloroacetic acid, however, are much less than normal. Examples of this type have been interpreted in the past as indicative of the fact that the solute is associated in the solution, but the conception of Hildebrand (*J. Amer. Chem. Soc.*, 1916, **38**, 1452) that a positive deviation from Raoult's law is consequent upon differences in the internal pressures of the two components of the solution

offers an alternative explanation. This point will be discussed later. The curve given by the compound, if this were completely dissociated in the solution into ester and acid, would be the sum of the depressions given by its components separately. This is shown as curve IV on the diagram. (For strict purposes of comparison, it may be noted,

FIG. 3.

System: ethyl acetate–acetic acid. Benzene as solvent.



I *Acetic acid.* II *Ethyl acetate* (●); *ideal curve* (○). III *Ethyl acetate+acetic acid (experimental).* IV *Sum of* I *and* II.

the deviation of the ideal freezing-point depression curve from linearity should be taken into account, and curve IV should fall slightly below the sum of curves I and II, but the error introduced by the simpler procedure here adopted is negligible throughout this work.) The actual curve obtained, curve III, lies considerably above curve IV, demonstrating that a large proportion of the compound is still existent as such in the system in spite of its reduced

concentration. The exact degree of dissociation at any given dilution cannot, however, be determined, since we have no means of knowing whether the curve for the undissociated compound follows the ideal or not. Most probably it would lie intermediately between the curves given by its two components, and we may therefore infer that the bulk of the compound is still undissociated when its concentration is diminished to 1—6 mol. %.

In view of the indefinite character of the results obtainable, the work in benzene solution was not extended to the additive compounds of benzyl benzoate and methyl succinate with trichloroacetic acid discussed in the preceding sections. It did seem of sufficient interest, nevertheless, to determine whether the existence of an ester–acid compound, already so unstable in the liquid state as to inhibit its direct isolation from the binary system by the freezing-point method, could still be established in dilute solution in an inert solvent. The results for the system ethyl acetate–acetic acid are given below and in Fig. 3.

TABLE V.

Freezing-point Depression Curves of Benzene (System: Ethyl Acetate–Acetic Acid).

Solutes.							
Acetic acid	Mol. %	0·993	2·75	3·93	4·84		
	$\Delta T°$	0·343	0·905	1·284	1·559		
Acetic acid + ethyl acetate	Mol. %	1·000	2·016	2·751	3·834	4·82	5·38
	$\Delta T°$	0·938	1·827	2·503	3·372	4·215	4·835

From Fig. 3 it is apparent that the freezing-point depressions induced by equimolecular quantities of ethyl acetate and acetic acid taken together are slightly smaller than those obtained by summing up the effects of the two separate components, an indication that some additive compound is still present. The degree of dissociation of this compound at any given dilution is again uncertain, owing to the abnormality of the acetic acid curve, but it is evidently much greater than that of the ethyl acetate–trichloroacetic acid compound, as might be expected with a weak acid as one component.

The Internal Pressure Factor in Freezing-point Depression Curves.

It remains to discuss briefly the abnormalities noted in the various systems examined. These, it will be found, all occur in systems in which we have a polar solute and a non-polar solvent, and in all cases the observed freezing-point depression is less than anticipated. Now Hildebrand (*loc. cit.*) has shown that an abnormally small freezing-point depression is a general characteristic of such systems, in which the internal pressures of the two components

in the liquid state are markedly different. While, therefore, association of the solute may occur to a minor extent in the cases of trichloroacetic acid and acetic acid in benzene, yet the abnormally small freezing-point depressions obtained must be ascribed, in the main, to the internal pressure factor.

The freezing-point depression curves of the ester–acid compounds with water as solute may be explained in the same way. We should certainly expect water to dissociate these compounds to a far greater degree than benzene, yet the two solutes give curves which are practically coincident. The curves ought to be widely divergent, apart from any question of instability of the solvent, since water and benzene have internal pressures so very far apart from each other that they cannot both be ideal solutes in the same liquid. Most probably, therefore, very extensive dissociation of the ester–acid compound on addition of water does occur, but the negative deviation from Raoult's law consequent thereupon is obscured by a simultaneous positive deviation from Raoult's law due to the internal pressure factor. Confirmation for this view will be found in the results of the succeeding article, in which the stability of ester–acid compounds in dilute aqueous solution is examined in detail.

Summary.

The stability of three ester–acid additive compounds on fusion has been investigated. The approximate degrees of dissociation are :

(*a*) Ethyl acetate–trichloroacetic acid (m. p. −26·8°); 12%.
(*b*) Benzyl benzoate–trichloroacetic acid (m. p. 13·6°); 35%.
(*c*) Methyl succinate–trichloroacetic acid (m. p. 8·3°); 4—6%.

These values refer to different temperatures (an unavoidable defect of the freezing-point method employed), but the order of stability is in accordance with previous work. Changes in degree of dissociation with temperature are presumably small. The molecular heats of fusion of the three compounds are 5170, 5660, and 9600 calories respectively.

In dilute benzene solution (at temperatures slightly above 0°) the compound ethyl acetate–trichloroacetic acid is still markedly stable, and the decomposition of such a weak complex as ethyl acetate–acetic acid is not complete.

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CCXXXVI.—*Additive Compounds in the Ternary System: Ester–Acid–Water.*

By JAMES KENDALL and CECIL VICTOR KING.

SEVERAL distinct lines of attack have been followed in this investigation, in the hope that the results obtained by converging upon the problem from different angles, together with the various suggestions derived from the simpler binary systems, might furnish greater opportunity for an advance. The freezing-point depression data which form the main part of the work are consequently discussed and correlated with conductivity and reaction velocity determinations at 0°. It is unfortunate that the extensive experimental data of previous investigators on certain of the systems studied cannot be employed to any considerable degree in this comparison, but the majority of such measurements refer to higher temperatures and are not readily reducible to molecular concentration units.

In this paper the four systems ethyl acetate–hydrochloric acid, ethyl acetate–trichloroacetic acid, ethyl acetate–chloroacetic acid, and ethyl acetate–acetic acid are examined in detail, with the idea of ascertaining how conditions vary when a representative ester is paired against a series of acids of widely divergent strengths.

Binary Systems Acid–Water and Ester–Water.

Systems of the type acid–water have already been critically investigated by Kendall, Booge, and Andrews (*J. Amer. Chem. Soc.*, 1917, **39**, 2303), and the general law has been deduced that compound formation increases with the strength of the acid. Little work has been done upon systems of the type ester–water. Griffith and Lewis (J., 1916, **109**, 80) have postulated an additive ester-water compound as an intermediate step in ester hydrolysis, but the freezing-point depression data of Rivett for ethyl acetate (*Z. physikal. Chem.*, 1912, **80**, 547), when recalculated on a molecular concentration basis, follow the ideal curve almost exactly. On account of this fact the opinion was expressed (*J. Amer. Chem. Soc.*, 1916, **38**, 1716) that ester–water compounds could not be formed in more than minute quantity. Our own freezing-point depression determinations for ethyl acetate, presented in Table I below (see also Fig. 1), are in complete accordance with those of Rivett, yet a more intensive study of the system leads us now to reverse our judgment.

Briefly, ethyl acetate is a "pseudo-ideal" solute in water, two opposing factors practically counterbalancing each other. The fact that ethyl acetate and water are only partly miscible (due to

internal pressure differences) precludes all possibility of a normal freezing-point depression curve; the experimental depressions should be considerably less than the ideal (see Hildebrand, "Solubility," A. C. S. Monograph Series, 1924; also p. 1777 of the preceding article). The only factor that could depress the curve back again to correspond with the ideal is extensive compound formation between ester and water, and there are several points which indicate that extensive compound formation actually does occur. Liquids which are partially miscible normally give absorption of heat on admixture, but heat is evolved, not absorbed, when ethyl acetate is dissolved in water. The rapid increase in the solubility of the ester as the temperature is lowered suggests that a compound is formed, the stability of which increases with falling temperature (Hildebrand, *loc. cit.*, p. 144). The fact that the density of the saturated solution at 0° is greater than unity (Seidell, "Solubilities of Inorganic and Organic Compounds," D. van Nostrand Co., 1919, p. 285) demonstrates that remarkable contraction accompanies admixture, and this contraction is most simply explained on the assumption of compound formation.

Other systems of the type R·CO·OR′–H_2O are now being examined to discover how these two opposing factors—internal pressure difference and compound formation—vary with the nature of the radicals R and R′. For the present, it suffices to know that all three possible binary systems (ester–acid, acid–water, and ester–water) give additive compounds, and it becomes necessary to determine to what extent these survive in the ternary system and whether any ternary compounds are formed.

Freezing-point Depression Determinations.

The freezing-point depression results obtained with water on addition of ethyl acetate, the four acids, and equimolecular quantities of ester and each acid taken together, are presented in Table I. The data for the hydrochloric and acetic acid systems are also given in Figs. 1 and 2, respectively.

At first the measurements for solutions containing both acid and ester were made at known time intervals after mixing, with the intention of extrapolating to zero time to correct for the change in freezing point due to hydrolysis. This procedure was, however, found to be unnecessary, as the freezing point in the most concentrated solution of the strongest acid did not vary more than a few thousandths of a degree in a whole hour. The experimental procedure was the same as that employed with benzene as solvent in the preceding article. The values given below are the results of duplicate measurements, checking to $\pm 0{\cdot}002°$.

TABLE I.

Freezing-point Depression Curves of Ester–Acid Solutions.

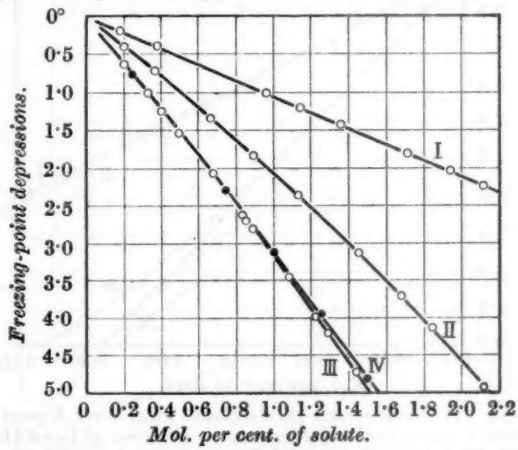
Solutes.							
Ethyl acetate	Mol. %	0·181	0·379	0·574	0·963	1·148	1·362
	$\Delta T°$ (obs.)	0·190	0·398	0·594	1·007	1·203	1·431
	$\Delta T°$ (ideal)	0·187	0·391	0·592	0·994	1·185	1·406
	Mol. %	1·718	1·945	2·134			
	$\Delta T°$ (obs.)	1·797	2·034	2·224			
	$\Delta T°$ (ideal)	1·773	2·007	2·202			
Hydrochloric acid	Mol. %	0·204	0·369	0·666	0·897	1·139	1·457
	$\Delta T°$	0·398	0·720	1·335	1·835	2·374	3·142
	Mol. %	1·686	1·851	2·136			
	$\Delta T°$	3·703	4·126	4·931			
Ethyl acetate + hydrochloric acid	Mol. %	0·209	0·335	0·409	0·499	0·681	0·838
	$\Delta T°$	0·626	1·008	1·247	1·525	2·099	2·637
	Mol. %	0·858	0·893	1·086	1·230	1·297	1·446
	$\Delta T°$	2·702	2·817	3·466	3·979	4·194	4·727
Trichloroacetic acid	Mol. %	0·277	0·528	0·765	1·002	1·264	1·439
	$\Delta T°$	0·530	0·994	1·451	1·884	2·373	2·697
	Mol. %	1·722	2·032	2·293	2·541		
	$\Delta T°$	3·223	3·791	4·256	4·697		
Ethyl acetate + trichloroacetic acid	Mol. %	0·176	0·259	0·409	0·554	0·728	0·856
	$\Delta T°$	0·510	0·748	1·187	1·592	2·063	2·434
	Mol. %	0·944	1·042				
	$\Delta T°$	2·651	2·869				
Chloroacetic acid	Mol. %	0·160	0·338	0·592	0·931	1·360	1·647
	$\Delta T°$	0·176	0·369	0·639	0·978	1·395	1·667
	Mol. %	1·755	1·999				
	$\Delta T°$	1·766	1·989				
Ethyl acetate + chloroacetic acid	Mol. %	0·249	0·473	0·593	0·904	1·256	1·314
	$\Delta T°$	0·525	0·988	1·227	1·826	2·448	2·548
	Mol. %	1·513	1·709	1·791			
	$\Delta T°$	2·866	3·153	3·264			
Acetic acid	Mol. %	0·537	0·902	1·341	1·624	1·871	2·393
	$\Delta T°$	0·556	0·952	1·381	1·663	1·916	2·442
	Mol. %	2·896					
	$\Delta T°$	2·944					
Ethyl acetate + acetic acid	Mol. %	0·176	0·303	0·437	0·819	0·957	1·161
	$\Delta T°$	0·373	0·634	0·917	1·667	1·941	2·353
	Mol. %	1·523	1·674	2·035	2·217	2·631	
	$\Delta T°$	3·042	3·315	3·919	4·202	4·775	

The significance of the data may be most readily appreciated by reference to the diagrams. In the hydrochloric acid system (Fig. 1), the freezing-point depressions induced by acid and ester taken together (curve III) are almost identical with the sum of the depressions induced by corresponding concentrations of the two separately (curve IV). Now if the ester–acid complex R·CO·OR′,HX were completely stable in solution, we should expect its curve to follow approximately the ethyl acetate (or ideal) curve (I) in the event of its being a non-electrolyte, or the hydrochloric acid curve (II) in the more probable event of its being a strong electrolyte giving the ions $[R·CO·OR′,H]^+$ and X^-.

An intermediate position between (I) and (II), or between (II) and (IV), would follow from partial dissociation. The actual position of the curve indicates, however, complete dissociation of the compound into its components, and also demonstrates that ternary complexes cannot exist in any significant quantity in the solution. (In point of fact, curve III lies very slightly below curve IV. This discrepancy may be explained, however, by taking into account the slight deviation of the ideal curve from linearity [compare p. 1775], accentuated in this case by hydration of the solutes.) To explain the total instability of the ester–acid compound in water solution we need only to consider that the

FIG. 1.

System: ethyl acetate–hydrochloric acid. Water as solvent.



I *Ethyl acetate (also ideal curve).* II *Hydrochloric acid.* III *Ethyl acetate + hydrochloric acid (experimental,* ○). IV *Sum of* I *and* II (●).

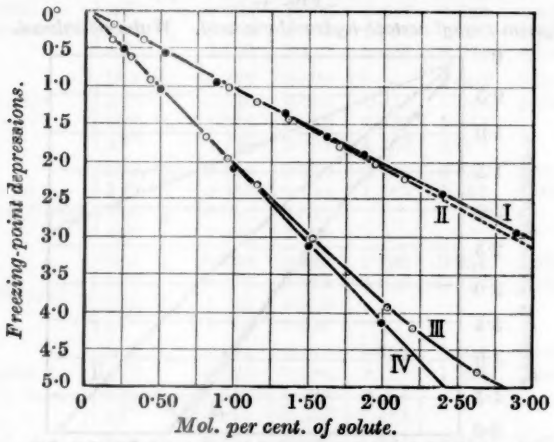
ester and the water function as rival bases, competing for the possession of the hydrochloric acid. Alone, each is able to furnish a stable additive compound (or oxonium salt); but in dilute aqueous solution the enormous excess of water and its more highly basic character lead to essentially complete destruction of the ester–acid complex.

In the acetic acid system (Fig. 2), on the other hand, the freezing-point depressions obtained with acid and ester together are, at the higher concentrations examined, appreciably less than the sum of those obtained with the two solutes separately. The same results are given by the trichloroacetic and chloroacetic acid systems, the difference at equivalent concentrations (*e.g.*, 1 mol. %) increasing with the strength of the acid. This might be argued to indicate

that a small fraction of the ester–acid complex does, after all, escape decomposition, the fraction increasing with the strength of the acid. On this basis, the results for the hydrochloric acid system alone would have to be regarded as abnormal. Alternatively, the three freezing-point depression curves in a system containing an organic acid may be considered as not strictly comparable, owing to differences in internal pressure and association factors. It is significant, in this connexion, that chloroacetic and acetic acids already give small positive deviations from Raoult's law in concentrated aqueous solution, before any addition of ester.

FIG. 2.

System: ethyl acetate–acetic acid. Water as solvent.



I *Acetic acid.* II *Ethyl acetate* (*prolonged as ideal curve beyond saturation*). III *Ethyl acetate* + *acetic acid* (*experimental*). IV *Sum of* I *and* II.

Before this question is discussed further, the conductivity and velocity of reaction results for equimolecular mixtures of ethyl acetate with the four acids will be presented. A final feature of the freezing-point depression curves may be noted here: the maximum concentration that can be investigated varies very remarkably in the four systems. It is not possible, of course, to carry out exact solubility measurements under the conditions of experiment, but the approximate molecular concentrations at which two liquid layers first persist, when equivalent quantities of ethyl acetate and acid are added to water at 0°, are as follows:

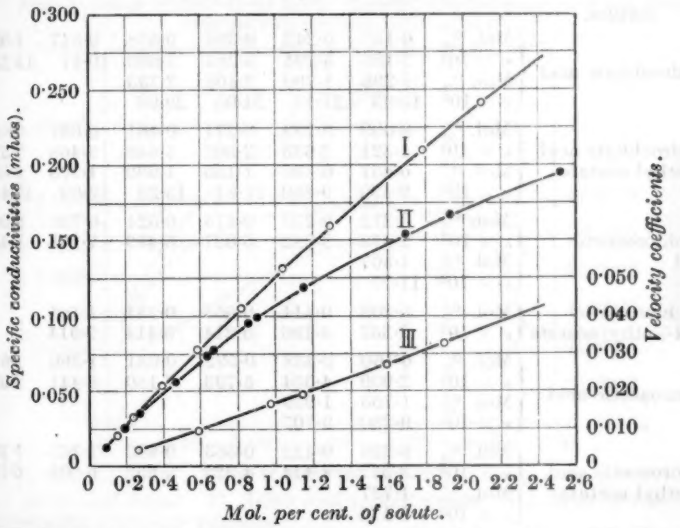
Ester alone.	Ester + HCl.	Ester + $CCl_3{\cdot}CO_2H$.	Ester + $CH_2Cl{\cdot}CO_2H$.	Ester + $CH_3{\cdot}CO_2H$.
2·2	2·55	1·1	1·75	2·75

It would be hazardous to offer even a tentative explanation of these solubility changes. If the second phase were fixed (as in

the case of a solid solute), an increase in solubility could be interpreted as indicative of compound formation. In the present instance, however, the saturating phase is not pure ethyl acetate, but a second liquid layer containing dissolved water and acid, so that no general comparison can be made. The run of the figures is certainly very curious, the strongest and weakest acids causing increased solubility and the intermediate acids decreased solubility. The 50% decrease of solubility in the presence of trichloroacetic acid, a substance perfectly miscible with both ester and water, is particularly mystifying.

FIG. 3.

System: ethyl acetate–hydrochloric acid. Specific conductivities and reaction velocities in aqueous solution at 0°.



I *Hydrochloric acid.* II *Hydrochloric acid + ethyl acetate.* III *Reaction velocities: equimolecular ester-acid solutions.*

Specific Conductivity Determinations.

A General Radio Co. audio-oscillator, giving a nearly pure sine-wave alternating current at a frequency of 1000 per second, was used as the source of current. With solutions of high resistance a sharper minimum was obtained by inserting a two-stage thermionic amplifier (compare Hall and Adams, *J. Amer. Chem. Soc.*, 1919, 41, 1515). The bridge was a Leeds and Northrup 4·7 metre circular slide-wire instrument, with resistance coils from 0·1 to 10,000 ohms. Baldwin type G telephones were employed.

The conductivity cells were of the Washburn dumb-bell type, with unplatinised electrodes. Their constants, 128·66 and 0·3694

respectively, were determined according to the directions of Kraus and Parker (*J. Amer. Chem. Soc.*, 1922, **44**, 2422). Small variable air condensers were used across the resistances to balance out the cell capacity. All measurements were made in a large bath of cracked ice and water, the temperature of which was constant at $-0{\cdot}02 \pm 0{\cdot}005°$. Conductivities taken at known time intervals after mixing the acid–ester solutions showed that in no case was it necessary to extrapolate back to zero time, hydrolysis at 0° being sufficiently slow to exercise no significant effect during the time of measurement.

TABLE II.

Specific Conductivities of Ester–Acid Solutions at 0°.

Solutes.							
Hydrochloric acid	Mol. %	0·157	0·242	0·396	0·588	0·817	1·056
	$\kappa \times 10^2$	2·158	3·294	5·283	7·693	10·47	13·23
	Mol. %	1·298	1·799	2·105	2·753		
	$\kappa \times 10^2$	15·93	21·12	24·05	29·68		
Hydrochloric acid + ethyl acetate	Mol. %	0·099	0·199	0·271	0·461	0·637	0·644
	$\kappa \times 10^2$	1·321	2·633	3·503	5·646	7·468	7·525
	Mol. %	0·857	0·899	1·155	1·699	1·923	2·521
	$\kappa \times 10^2$	9·490	9·860	11·81	15·29	16·69	19·44
Trichloroacetic acid	Mol. %	0·212	0·270	0·475	0·524	0·738	0·907
	$\kappa \times 10^2$	2·473	3·082	5·027	5·489	7·235	8·448
	Mol. %	1·507					
	$\kappa \times 10^2$	11·77					
Trichloroacetic acid + ethyl acetate	Mol. %	0·208	0·414	0·553	0·751	1·104	
	$\kappa \times 10^2$	2·357	4·196	5·214	6·414	7·914	
Chloroacetic acid	Mol. %	0·160	0·338	0·592	0·931	1·360	1·647
	$\kappa \times 10^3$	2·909	4·354	5·793	7·180	8·441	9·080
	Mol. %	1·755	1·999				
	$\kappa \times 10^3$	9·290	9·707				
Chloroacetic acid + ethyl acetate	Mol. %	0·228	0·422	0·563	0·883	1·165	1·393
	$\kappa \times 10^3$	3·357	4·414	4·922	5·652	6·004	6·129
	Mol. %	1·727					
	$\kappa \times 10^3$	6·175					
Acetic acid	Mol. %	0·205	0·390	0·619	0·817	1·071	1·174
	$\kappa \times 10^4$	3·420	4·644	5·765	6·474	7·264	7·519
	Mol. %	1·397	1·744	2·126	2·911		
	$\kappa \times 10^4$	8·063	8·731	9·279	10·11		
Acetic acid + ethyl acetate	Mol. %	0·169	0·306	0·557	0·861	1·112	1·412
	$\kappa \times 10^4$	2·962	3·736	4·720	5·315	5·563	5·699
	Mol. %	1·795	2·181	2·366	2·723		
	$\kappa \times 10^4$	5·698	5·589	5·506	5·306		

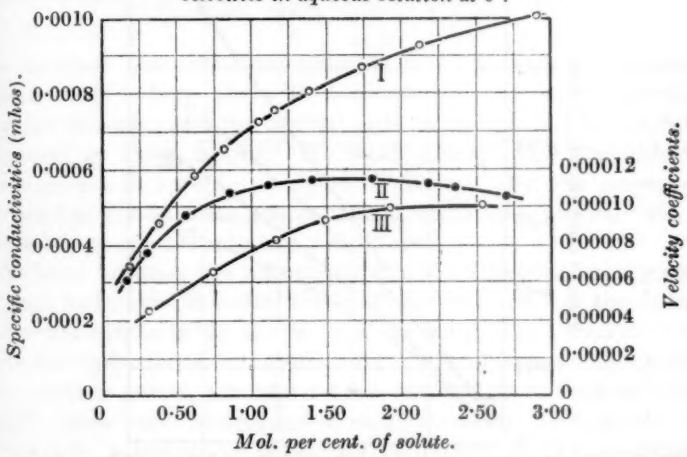
The curves for the hydrochloric and acetic acid systems are shown in Figs. 3 and 4. It will be seen that the addition of an equivalent quantity of ethyl acetate brings about a considerable diminution in the specific conductivity of the acid solutions, the effect being more pronounced the higher the concentration. In the acetic acid system, the reduction is actually sufficient to cause a decrease in the specific conductivity at concentrations above

1·6 mols. %. The percentage reduction increases as the acidic strength decreases, the lowering of specific conductivity for the four systems at 1·0 mol. % being: HCl, 16%; $CCl_3 \cdot CO_2H$, 18%; $CH_2Cl \cdot CO_2H$, 23%; $CH_3 \cdot CO_2H$, 24%. (The increase in the volume of the solution due to the addition of ester at this concentration, it may be noted, is less than 5%. The reduction in specific conductivity, therefore, is not simply due to dilution.)

This phenomenon has been noted previously by Griffith and Lewis (*loc. cit.*). The most obvious means of accounting for the observed decrease is to assume compound formation of ester with acid in the solution. If the ester–acid complex R·CO·OR′,HX

FIG. 4.

System: ethyl acetate–acetic acid. Specific conductivities and reaction velocities in aqueous solution at 0°.



I *Acetic acid, alone.* II *Acetic acid + ethyl acetate.* III *Reaction velocities: equimolecular acid–ester solutions.*

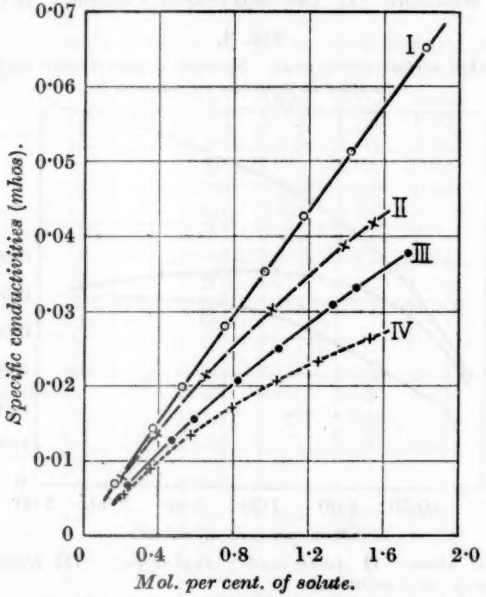
remained non-ionised, then its formation would lower the concentrations of both H^+ and X^-, whilst if it were an electrolyte the main factor would be the replacement of the rapidly-moving ion H^+ by the less mobile complex $[R \cdot CO \cdot OR',H]^+$. Two alternative explanations, however, must also be considered: (*a*) the addition of ester may cause a decrease in the dielectric constant of the solution and so reduce the extent of ionisation of the acid, or (*b*) the addition of ester may simply decrease the mobility of the ions without changing their nature (compare alcohol–water mixtures, Godlewski, *Z. physikal. Chem.*, 1905, **51**, 751).

None of these three explanations is in entire harmony with the freezing-point depression results already recorded for the same systems. The extent of compound formation demanded by the

first is much greater than that indicated by the freezing-point curves for the three organic acids, while the hydrochloric acid data are in direct conflict with any assumption of ester–acid complex survival in the system. Under the second explanation, not only are the observed freezing-point depression curves abnormal in the case of the two strong acids, but it is necessary to assume an enormous decrease in the dielectric constant for the addition of a small amount of ester. The following experiments may be regarded

FIG. 5.

Specific conductivities of ethyl acetate–salt solutions at 0°.



I *Potassium chloride, alone.* II *Potassium chloride + ethyl acetate.* III *Potassium acetate, alone.* IV *Potassium acetate + ethyl acetate.*

as definitely eliminating these two hypotheses, and thereby increasing the likelihood that the third is, in general, valid.

The effect of addition of ester on the specific conductivities of neutral salt solutions may first be considered. Potassium chloride and potassium acetate were selected as typical derivatives of a strong and a weak acid respectively, and the determinations, carried out exactly as in the case of the acid solutions, are summarised in Table III and Fig. 5.

It is evident from Fig. 5 that the addition of ester decreases the specific conductivity of a neutral salt solution just as effectively as it does that of an acid solution. At a concentration of 1·0 mol. %

TABLE III.

Specific Conductivities of Ester–Salt Solutions at 0°.

Solutes.							
Potassium chloride	Mol. %	0·167	0·372	0·523	0·755	0·965	1·172
	$\kappa \times 10^2$	0·688	1·424	1·969	2·798	3·535	4·259
	Mol. %	1·424	1·820				
	$\kappa \times 10^2$	5·132	6·521				
Potassium chloride + ethyl acetate	Mol. %	0·204	0·390	0·645	1·000	1·396	1·540
	$\kappa \times 10^2$	0·780	1·388	2·131	3·027	3·892	4·183
Potassium acetate	Mol. %	0·245	0·479	0·597	0·829	1·046	1·345
	$\kappa \times 10^2$	0·688	1·270	1·547	2·063	2·507	3·091
	Mol. %	1·458	1·735				
	$\kappa \times 10^2$	3·298	3·775				
Potassium acetate + ethyl acetate	Mol. %	0·215	0·360	0·575	0·797	1·039	1·256
	$\kappa \times 10^2$	0·587	0·919	1·344	1·717	2·063	2·333
	Mol. %	1·532					
	$\kappa \times 10^2$	2·628					

the decrease for potassium chloride is 17%, and for potassium acetate 18%. Now there is certainly no compound formation between the ester and the neutral salts in the solution to the extent indicated by these figures. We must consequently conclude that the decrease in specific conductivity induced by the presence of the ester is due to some general effect, quite unconnected with the formation of specific additive compounds.

A choice between the second and the third hypothesis is possible through hydrogen-ion concentration measurements. If the decrease in specific conductivity is due to a lowering of the dielectric constant, the hydrogen-ion concentration of the solution should diminish when ester is added, whereas a mere diminution in ionic mobilities should leave the hydrogen-ion concentration unchanged. Unfortunately, attempts to obtain direct hydrogen-ion concentration determinations by the hydrogen electrode method gave inconclusive results, since it was found that the potential of the hydrogen-ion electrode in a freshly prepared acid–ester solution at 0° was practically the same as in the same solution after hydrolysis had run to completion, or as in a solution containing equivalent quantities of the hydrolysis products, acetic acid and ethyl alcohol. Apparently the hydrolysis is catalysed so rapidly by the platinum black that in the immediate vicinity of the electrode equilibrium conditions are reached almost instantaneously. This point is being studied further, with modifications of method.

The matter may be decided indirectly, however, by determining the effect of the addition of ethyl acetate on the rate of sucrose inversion in an acid solution. Previous experiments by Coppadoro (*Gazzetta*, 1901, **31**, i, 425) with methyl acetate suggested that a considerable reduction does occur, but Henri and des Bancels

(*Compt. rend. Soc. Biol.*, 1901, **53**, 784) and Griffith and Lewis (*loc. cit.*) agree that the same ester exercises practically no influence. With ethyl acetate the following results at 0° were obtained:

Mol. % of solutes.	Inversion constant.
I. Sucrose 1·5; HCl 1·5	0·01045
II. Sucrose 1·5; HCl 1·5; ethyl acetate 1·5	0·01035

The inversion was followed in a Schmidt and Haensch polarimeter, reading to 0·01°. The solutions were placed in a 220 mm. tube, immersed in a bath kept at 0 ± 0·01° and fitted as described by Nelson and Beegle (*J. Amer. Chem. Soc.*, 1919, **41**, 559). The inversion constants given above have an accuracy of ± 1%, so it is clear that addition of ester induces practically no change in the rate of inversion and presumably, therefore, no significant change in the hydrogen-ion concentration of the solution. Diminution of ionic mobility is consequently to be regarded as the probable cause of the lowering in specific conductivity recorded in Tables II and III.

Determinations of Velocity of Hydrolysis.

The rates of hydrolysis of ethyl acetate at 0° in the presence of equivalent quantities of the four acids up to the saturation concentration are given in Table IV below. The curves for the hydrochloric and acetic acid systems are shown also in Figs. 3 and 4. The course of the hydrolysis was followed by the usual method of withdrawing samples from the bath at intervals and titrating against potassium hydroxide, standardised against hydrochloric acid and free from carbonate. The time required for solutions of the weaker acid to reach equilibrium varied from 1 to 8 weeks. In a few instances, it was necessary to determine the end value by raising the temperature to 25° for a time and then returning to 0° for a week or so to obtain a final adjustment. In view of the very small change with temperature of the position of the equilibrium point in ester hydrolysis, no significant error could be introduced by this hastening of the reaction.

The variation in the rate of hydrolysis, k, for the three stronger acids approximated 1% in a single run. Duplicate runs agreed also within this limit. For the acetic acid solutions, where hydrolysis proceeded extremely slowly, the variation was as much as 2—3%.

For simplicity, the reaction is treated here as if it were of a simple unimolecular type, and all the constants are calculated on that basis. Griffith and Lewis (J., 1908, **109**, 67) have shown, it is true, that the hydrolysis must finally be regarded as bimolecular and reversible, but space does not permit us to discuss in

detail here the complete analysis of our data according to their equations. This matter will be taken up in full in a later paper; it will suffice to state at this stage that the general conclusions developed below are substantially unchanged under the more rigid method of calculation.

TABLE IV.

Reaction Velocities in Ester–Acid Solutions at 0°.

Solutes.							
Ethyl acetate + hydrochloric acid	Mol. %	0·271	0·598	0·970	1·151	1·597	1·909
	$k \times 10^2$	0·440	0·966	1·62	1·91	2·74	3·26
Ethyl acetate + trichloroacetic acid	Mol. %	0·293	0·615	0·816	0·922	1·089	
	$k \times 10^2$	0·440	0·902	1·15	1·29	1·45	
Ethyl acetate + chloroacetic acid	Mol. %	0·294	0·670	0·923	1·240	1·412	1·677
	$k \times 10^3$	0·484	0·754	0·855	0·952	0·984	1·04
Ethyl acetate + acetic acid	Mol. %	0·316	0·742	1·170	1·496	1·926	2·541
	$k \times 10^4$	0·444	0·644	0·829	0·934	0·987	1·015

From the velocity coefficient curves for the hydrochloric acid system in Fig. 3 it will be seen that the rate of hydrolysis increases much more rapidly than the specific conductivity, and more rapidly indeed than the molecular concentration of the acid. This may be interpreted in two ways. First of all, it may be regarded as indicative of the fact, already noted in the freezing-point depression curve, that the "activity" of the hydrogen ion increases more rapidly than the acid concentration, even when this is expressed in molecular units. Alternatively, it may be construed, according to the theory that the non-solvated hydrogen ion alone is catalytically active (recently revived by Rice, *J. Amer. Chem. Soc.*, 1923, **45**, 2808), as signifying that the non-hydrated fraction of the hydrogen ion increases steadily as the concentration of the two solutes is increased, owing to the diminishing concentration of free water present in the solution. The two statements are not mutually exclusive, in all probability, but merely different methods of expressing the same situation.

The curve for the acetic acid system (Fig. 4), on the contrary, shows a velocity coefficient increasing less rapidly than the specific conductivity of the acid in the absence of ester, although more rapidly than the specific conductivity of the acid in the presence of ester. A maximum reaction velocity is obtained at about 2·4 mols. %. Just as in the case of the freezing-point depression data, the curves for the trichloroacetic acid and chloroacetic acid systems are similar in character to that for acetic acid, although their rate of change of slope becomes less and less rapid as the strength of the acid is increased.

Further discussion of the rate of reaction curves would not be

profitable at this point, inasmuch as no quantitative comparison can be made between them and the specific conductivity curves until density and viscosity data for the solutions are available. These data will also render it possible to transpose the measurements here recorded to volume concentration units, and to utilise the results of previous workers. Whilst the conclusions drawn from this investigation are only preliminary and qualitative, yet the use of molecular concentration ratios has enabled several important deductions to be made. The main points of the work may be summarised briefly as follows:

Summary.

(1) Ethyl acetate gives a "pseudo-ideal" freezing-point depression curve in aqueous solution, and must consequently be extensively hydrated.

(2) The freezing-point depression caused by equivalent quantities of ethyl acetate and hydrochloric acid taken together is greater than the sum of the depressions due to the two separately. It follows that ternary complexes and ester–acid additive compounds are not existent in significant quantity in the aqueous solution. This conclusion is supported by specific conductivity data.

(3) Although the freezing-point depression curves obtained for trichloroacetic, chloroacetic, and acetic acids with ethyl acetate appear to indicate the survival of some ester–acid complex, yet the specific conductivity results in these systems also demonstrate decisively that no appreciable fraction actually persists. The freezing-point curves with these organic acids are presumably not strictly comparable, owing to internal pressure and association changes.

(4) The specific conductivity of a neutral salt, as well as of an acid, in aqueous solution is lowered by the addition of ethyl acetate. This lowering is due to diminished ionic mobilities.

(5) The rate of hydrolysis of ethyl acetate in the presence of hydrochloric acid in equivalent quantity increases more rapidly than the molecular concentration of the acid. With weaker acids, the rate of hydrolysis increases less rapidly. In fact, the curve for acetic acid shows a maximum rate near the saturation point.

(6) The solubility of ethyl acetate in water at 0° varies very remarkably when electrolytes are also present in equivalent quantity.

(7) The rate of inversion of sucrose in hydrochloric acid solution at 0° is not affected by the addition of ethyl acetate. Inasmuch as the rate of ester hydrolysis is greatly increased by the addition of sucrose, it is clear that the mechanisms of the two reactions must be fundamentally different.

In conclusion it must be emphasised that, although it has been demonstrated that ester–acid additive compounds and ternary complexes of these with water do not exist in quantity in aqueous solution, yet this cannot be considered as proof that such compounds do not constitute intermediate steps in the reaction. An infinitesimal quantity of a compound at any one time would suffice for this purpose, its very instability serving, indeed, as a potent factor in the catalysis. The minimal extent to which these ester–acid compounds survive precludes further study of them by the freezing-point depression method, but valuable results are promised from a more intensive study of compounds of the type ester–water. The factors influencing the stability of compounds of this general type $R{\cdot}CO_2R',H_2O$ in the presence of an acid HX as R, R', and X are varied, will be discussed in a forthcoming paper.

COLUMBIA UNIVERSITY,
NEW YORK CITY. [*Received, May 11th*, 1925.]

CCXXXVII.—*The Preparation of Phthalamic Acids and their Conversion into Anthranilic Acids.*

By ERNEST CHAPMAN and HENRY STEPHEN.

PHTHALAMIC acid results from two additive reactions: (*a*) from water and phthalimide (Aschan, *Ber.*, 1886, **19**, 1403), and (*b*) from ammonia and phthalic anhydride (Auger, *Bull. Soc. chim.*, 1888, **49**, 349).

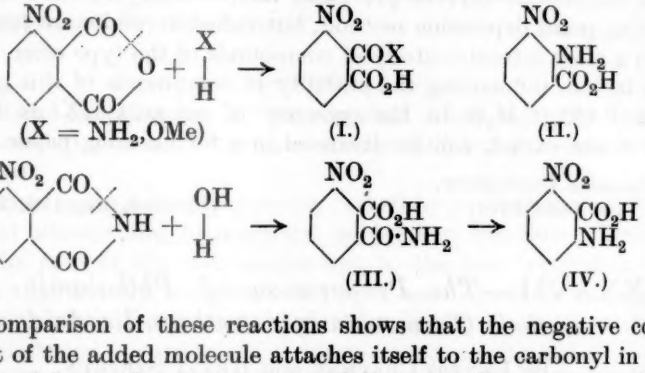
The modification and extension of Auger's method now described show that reaction (*b*) affords phthalamic acids in excellent yield. Since these acids react smoothly with sodium hypochlorite, anthranilic acids become readily accessible. Anthranilic acid and 4 : 5-dibromoanthranilic acid are readily obtained from the corresponding anhydrides.*

Unsymmetrical phthalic anhydrides, according to reaction (*b*), may give rise to one or both of two isomeric phthalamic acids, and it is of interest to discover (1) which amic acid is produced, alone or in the greater quantity, and (2) whether this amic acid is the same as that formed as chief product from the corresponding imide according to (*a*). The behaviour of 3- and 4-nitrophthalic anhydrides has been investigated from this point of view.

3-Nitrophthalic anhydride yielded exclusively 3-nitrophthalamic acid (I) ($X = NH_2$), which gave, in 90% yield, the 3-nitroanthranilic acid (II) obtained in small yield by Hübner by treatment of

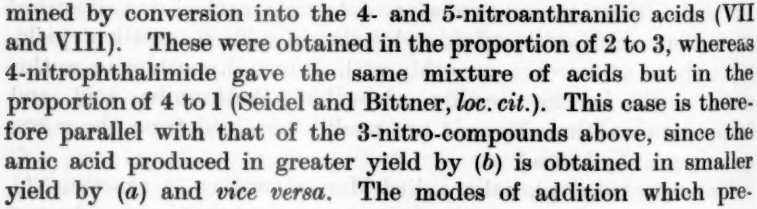
* The carboxyl group of phthalamic and anthranilic acids is numbered 1 and the amide or amine group 2.

" β-nitrosalicylic ester " with ammonia (*Annalen*, 1879, **195**, 37). Since 3-nitrophthalimide is converted by Hofmann's method almost entirely into 6-nitroanthranilic acid (IV) (Seidel, *Ber.*, 1901, **34**, 4352; Seidel and Bittner, *Monatsh.*, 1902, **23**, 415; Kahn, *Ber.*, 1902, **35**, 472), its preliminary hydrolysis must yield 6-nitrophthalamic acid (III).* The addition of methyl alcohol to 3-nitrophthalic anhydride is similar to that of ammonia (compare Wegscheider and Lipschitz, *Monatsh.*, 1900, **21**, 796).

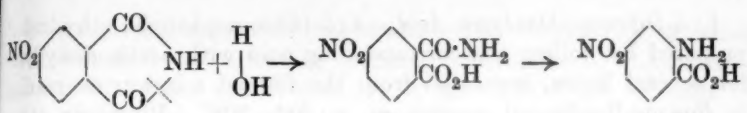


A comparison of these reactions shows that the negative component of the added molecule attaches itself to the carbonyl in the ortho-position to the nitro-group, and fission in all cases takes place at the same bond.

4-Nitrophthalic anhydride treated according to (*b*) gave an inseparable mixture of 4- and 5-nitrophthalamic acids (V and VI). The orientation and relative amounts of these acids were determined by conversion into the 4- and 5-nitroanthranilic acids (VII and VIII). These were obtained in the proportion of 2 to 3, whereas 4-nitrophthalimide gave the same mixture of acids but in the proportion of 4 to 1 (Seidel and Bittner, *loc. cit.*). This case is therefore parallel with that of the 3-nitro-compounds above, since the amic acid produced in greater yield by (*b*) is obtained in smaller yield by (*a*) and *vice versa*. The modes of addition which predominate in each reaction are as follows:



* Bogert and Boroschek (*J. Amer. Chem. Soc.*, 1901, **23**, 740) prepared this acid by the action of baryta on 3-nitrophthalimide, but wrongly described it as 3-nitrophthalamic acid. Kahn (*ibid.*, p. 3866) proved conclusively that it was 6-nitrophthalamic acid identical with the acid obtained by the action of ammonia on " 3-nitrophthal-β-methyl ester."



(V.) (VII.)

Here the negative components of the added molecules become attached to the carbonyl in the *para*-position relatively to the nitro-group.

In each of the cases considered, the course of the reactions corresponds with that observed with camphoric anhydride and camphorimide, the former with ammonia (reaction *b*) giving α-camphoramic acid, whilst the latter on alkaline hydrolysis (reaction *a*) gives β-camphoramic acid (see Lapworth, "On the Constitution of Camphor," *Brit. Assoc. Reports*, Section B, 1900, p. 6).

Experimental.

Phthalamic Acid.—Phthalic anhydride (60 g.), added gradually with stirring to warm aqueous ammonia (90 c.c.; d 0·88), dissolved readily with considerable evolution of heat, and *ammonium phthalamate* separated in fine, white crystals, the amount increasing on cooling (yield 70 g.; 94%) (Found: NH_3, 18·7. $C_8H_{10}O_3N_2$ requires NH_3, 18·4%). The salt was readily soluble in water, and was converted into phthalimide at about 200° without fusion. Phthalamic acid was obtained by treating the ammonium salt (30 g.) in cold water (30 c.c.) with a slight excess of the equivalent quantity of concentrated hydrochloric acid (20 c.c.) and washing the crystalline paste produced with cold water until it was free from chloride (yield 22 g.; 81%). The acid melted at 149° with loss of water, solidified at 155°, and remelted at 231° (phthalimide). Aschan (*loc. cit.*) and Auger (*loc. cit.*) give m. p. 149° and 140° respectively. Aqueous solutions of the acid are more stable at the ordinary temperature than would be expected from Aschan's statements.

Anthranilic Acid from Phthalamic Acid.—The "standard sodium hypochlorite solution" employed in this and all other cases to be described contained 47 g. of sodium hypochlorite and 50 g. of sodium hydroxide per litre.

Well-powdered phthalamic acid (20 g.) was gradually added to the stirred, cooled standard hypochlorite solution (200 c.c.), which became dark reddish-brown. Sodium hydroxide (10 g.) dissolved in water (50 c.c.) was now added, the mixture warmed at 80° for a few minutes, cooled, and acidified with acetic acid. The anthranilic acid isolated by means of copper acetate and liberated from the copper salt with hydrogen sulphide melted at 145°.

4 : 5-*Dibromophthalamic Acid.*—4 : 5-Dibromophthalic anhydride,* prepared by boiling the corresponding acid with acetic anhydride for several hours, separated from the filtered solution on cooling in fine, buff-coloured needles, m. p. 204—208°. Blümbein (*Ber.*, 1884, **17**, 2490) gives m. p. 208°, Lesser and Weiss (*Ber.*, 1913, **46**, 3937) give 214—215°. *Ammonium* 4 : 5-*dibromophthalamate* was obtained in pale brown crystals (15·5 g.; 91%) by treating the anhydride (15 g.) with concentrated aqueous ammonia (22 c.c.). On heating, it partly melted at 227° with loss of water and ammonia, resolidified a few degrees higher, and remelted at 238—242° (the m. p. of 4 : 5-dibromophthalimide is given as 242—245° by Bruck, *Ber.*, 1901, **34**, 2741, and as 245—246° by Lesser and Weiss, *loc. cit.*; see also below). 4 : 5-*Dibromophthalamic acid* was obtained from the ammonium salt by addition of acid (yield 93%) (Found: Br, 49·6. $C_8H_5O_3NBr_2$ requires Br, 49·5%). It softened with loss of water at 215—216°, being converted into the imide. Its aqueous solution reacted acid to litmus.

4 : 5-*Dibromophthalimide* was obtained in glistening yellow needles, m. p. 242—243° (Found: Br, 52·85. Calc., Br, 52·4%) by fusing the above amic acid and crystallising the product from alcohol.

4 : 5-*Dibromoanthranilic Acid.*—Dibromophthalamic acid (10 g.; 1 mol.) was added as before to standard hypochlorite solution (50 c.c.), and the yellow solution, after addition of sodium hydroxide (3 g.; 2 mols.) in water (20 c.c.), warmed to 80°, the colour becoming deep red. The 4 : 5-dibromoanthranilic acid precipitated from the solution, when cold, by a slight excess of hydrochloric acid crystallised from dilute alcohol as a pale brown powder, m. p. 224° (decomp.) (8·5 g.; 94%) (Found: Br, 54·4. Calc., Br, 54·2%). Lesser and Weiss (*loc. cit.*) give m. p. 228—229°. The acid is almost insoluble in cold water, slightly soluble in hot water, and dissolves in the usual organic solvents except benzene, chloroform, and ligroin.

Treatment of the acid with acetic anhydride gave 4 : 5-*dibromo*-2-*acetylaminobenzoic acid*, fine, buff-coloured needles from dilute alcohol, m. p. 240° (Found: Br, 47·3. $C_9H_7O_3NBr_2$ requires Br, 47·4%). Lesser and Weiss (*loc. cit.*, p. 3944) state that they obtained the acetyl derivative of the anhydride of the acid, m. p. 184—185°.

* Anhydrides of dibasic acids are conveniently and rapidly prepared in almost quantitative yield as follows. The finely powdered, dry sodium hydrogen salt (1 mol.) is warmed with thionyl chloride (3 mols.) for ½ hour, and the excess of thionyl chloride removed by distillation. The residue of anhydride and sodium chloride is boiled with benzene, and the solution filtered, the pure anhydride crystallising from the filtrate.—H. S.

3- *and* 4-*Nitrophthalic Anhydrides*.—The corresponding acids were obtained by nitrating phthalic anhydride by Lawrence's method (*J. Amer. Chem. Soc.*, 1920, **42**, 1872). An attempt to convert the 4-nitro-acid into its anhydride by heating at 165—168° for 3 hours as described by Lawrence (*loc. cit.*) proved unsatisfactory, the product containing much unchanged acid. Both anhydrides were finally obtained by fusing the acids and then reducing the pressure to 22 mm. The temperature (thermometer in the liquid), 210—230° for the 3-nitro-acid and 170—180° for the 4-nitro-acid, was maintained for 1 hour. The brown melts crystallised on cooling, and after recrystallisation from acetic anhydride or acetyl chloride, 3-nitro- and 4-nitro-phthalic anhydrides were obtained which melted at 163—164° and 115°, respectively, as stated by Lawrence.

3-*Nitrophthalamic Acid*.—The ammonium salt and the acid were obtained from the anhydride (30 g.) and concentrated aqueous ammonia (45 c.c.) by the methods previously described (yield 87%). The *ammonium* salt consisted of fine, white needles, m. p. 172° (decomp.), giving 3-nitrophthalimide, m. p. 217—218° (Bogert and Boroschek, *loc. cit.*, m. p. 215—216°; Kahn, *Ber.*, 1902, **35**, 471, m. p. 216°). 3-*Nitrophthalamic acid* softens with loss of water at 168—174°, being converted into the imide. It is sparingly soluble in cold and readily in hot water.

3-*Nitroanthranilic Acid*.—Finely powdered 3-nitrophthalamic acid (10 g.; 1 mol.) was treated with 75 c.c. of standard hypochlorite solution (1 mol. NaOCl) in the usual way, and sodium hydroxide (4 g.; 2 mols.), dissolved in water (10 c.c.), was added to the yellow solution. When the mixture was warmed at 80°, its colour gradually became brick-red and a bright red precipitate of sodium 3-nitroanthranilate separated. Sufficient water was added to the cooled mixture to dissolve the salt, and treatment with a slight excess of concentrated hydrochloric acid precipitated 3-nitroanthranilic acid as a bright yellow, crystalline powder (7·8 g.; 90%). The acid was obtained in fine, yellow needles, m. p. 208—209°, from hot water (Hübner, *loc. cit.*, gives m. p. 204°); in other respects the properties of the acid agree with those described by Hübner. Reduction of the acid with stannous chloride showed no indication of the formation of a derivative of *m*-phenylenediamine, and hence the absence of 6-nitroanthranilic acid.

3-*Nitro*-2-*acetylaminobenzoic acid*, obtained by boiling the above acid (2 g.) with acetic anhydride (4 c.c.) for 5 minutes, crystallised from hot water or acetic acid in bright yellow, silky needles, m. p. 180—181° (Found: N, 12·6. $C_9H_8O_5N_2$ requires N, 12·5%).

4- *and* 5-*Nitrophthalamic Acids*.—A mixture of the ammonium

salts of these acids was obtained by dissolving 4-nitrophthalic anhydride (60 g.) in warm aqueous ammonia (90 c.c.). The product (50 g.), consisting of fine, white needles, melted at 190—192° with decomposition, solidified, and remelted at 197—198°, having been converted into the imide (Bogert and Boroschek, *loc. cit.*, and Seidel and Bittner, *loc. cit.*, give m. p. of 4-nitrophthalimide as 197° and 202°, respectively). The mixture of 4- and 5-nitrophthalamic acids was obtained in almost theoretical yield by addition of concentrated hydrochloric acid (40 c.c.) to the ammonium salts (48 g.) in water (60 c.c.). Attempts to separate the acids were unsuccessful. The mixture melted at 150—155° with loss of water, resolidified and remelted at 198°, since both acids yield 4-nitrophthalimide.

4- *and* 5-*Nitroanthranilic Acids.*—A mixture of these acids was obtained by treating the above mixture of phthalamic acids (35 g.) with standard hypochlorite solution (266 c.c.) as described in the previous case. Acidification of the resulting red solution gave a mixture (22 g.; 73%) of yellow and orange particles, m. p. 250—260° (decomp.). A portion of the mixture (15 g.) was extracted in a Soxhlet apparatus for 2 days with boiling xylene, which became orange-red. The insoluble, pale yellow residue of 5-nitroanthranilic acid, amounting to 60% of the original mixture, crystallised from dilute alcohol in glistening, yellow needles, m. p. 280°, agreeing with m. p. given by Seidel and Bittner (*loc. cit.*). The m. p. of 5-nitroanthranilic acid is also variously given as follows: 263° (Hübner, *loc. cit.*); 270° (Rhalis, *Annalen*, 1879, **198**, 112); 261—263° (Kratz, *J. pr. Chem.*, 1896, **53**, 222); 263° (Rupe, *Ber.*, 1897, **30**, 1097); 269·5° (Ullmann and Uzbachian, *Ber.*, 1903, **36**, 1802). The acid showed the characteristic reactions described in the literature for 5-nitroanthranilic acid, and was converted into 5-nitro-2-acetylaminobenzoic acid, melting at 216—217°, by boiling with acetic anhydride. Seidel and Bittner (*loc. cit.*) and Ullmann and Uzbachian (*loc. cit.*) give, respectively, 214—215° and 221° as the melting point of the acetyl derivative.

The xylene solution obtained above left on evaporation a deep orange, flaky mass (40% of the original mixture) of 4-nitroanthranilic acid containing a little of its isomeride. Attempts to purify the acid by repeated crystallisation from alcohol as described by Seidel and Bittner (*loc. cit.*) were unsuccessful, as the final product melted indefinitely between 237—240°, and was evidently still a mixture. It was therefore converted into the acetyl derivative by boiling with acetic anhydride for a few minutes. The crude product melted at 190—195°, but after crystallising several times from dilute alcohol, 4-nitro-2-acetylaminobenzoic acid was obtained in long,

slender needles, m. p. 217° (Seidel and Bittner, *loc. cit.*, give 188°; Wheeler and Barnes, *Amer. Chem. J.*, 1898, **20**, 229, give 215°). A solution of the acetyl compound in a small quantity of hot alcohol was boiled with a few c.c of concentrated hydrochloric acid; on cooling, pale yellow needles of the hydrochloride of 4-nitroanthranilic acid separated.

The hydrochloride was dissociated by water and the 4-nitroanthranilic acid produced crystallised from dilute alcohol in stout, deep orange prisms, m. p. 269° (Wheeler and Barnes, *loc. cit.*, Wheeler and Johns, *Amer. Chem. J.*, 1910, **44**, 443, and Seidel, *Ber.*, 1901, **34**, 4352, give the m.p. of 4-nitroanthranilic acid as 264°). 4-Nitroanthranilic acid was difficultly soluble in hot water, and on reduction with stannous chloride and hydrochloric acid gave an indication of the formation of a derivative of *m*-phenylenediamine.

It is desired to acknowledge a grant made to one of us (E. C.) by the Department of Scientific and Industrial Research, which enabled him to participate in this work.

THE UNIVERSITY, MANCHESTER. [*Received, May 19th*, 1925.]

CCXXXVIII.—*Derivatives of δ-o-Aminobenzoylvaleric Acid.*

By MARGARET JOYCE PATERSON and SYDNEY GLENN PRESTON PLANT.

THE acid, m. p. 129°, obtained by Perkin and Plant (J., 1923, **123**, 678) and thought to be δ-*o*-aminobenzoylvaleric acid,

$$NH_2 \cdot C_6H_4 \cdot CO \cdot [CH_2]_4 \cdot CO_2H,$$

has been converted into δ-*o*-hydroxybenzoylvaleric acid, identical with the compound prepared by von Braun (*Ber.*, 1922, **55**, 3761) by the oxidation of hexahydrodiphenylene oxide, and its constitution thus proved.

δ-*o*-Aminobenzoylvaleric acid cannot be made to yield a phenylhydrazone, oxime, or semicarbazone under the usual conditions, but the corresponding derivatives of δ-*o*-hydroxybenzoylvaleric acid are readily obtained.

δ-*o*-Benzoylaminobenzoylvaleric acid is converted by alkalis into δ-*o*-aminobenzoylvaleric acid and a small quantity of γ-4-hydroxy-2-phenylquinoline-3-butyric acid (Perkin and Plant, *loc. cit.*). We now find that δ-o-*acetylaminobenzoylvaleric acid* gives better yields of the corresponding γ-4-*hydroxy*-2-*methylquinoline*-3-*butyric acid* as well as some δ-*o*-aminobenzoylvaleric acid. δ-o-*Formylaminobenzoylvaleric acid*, on hydrolysis under various

conditions, gave exclusively δ-*o*-aminobenzoylvaleric acid, no trace of a quinoline derivative being detected.

EXPERIMENTAL.

δ-o-*Hydroxybenzoylvaleric Acid.*—The diazo-solution prepared from δ-*o*-aminobenzoylvaleric acid (4 g.) in concentrated hydrochloric acid (20 c.c.) and water (40 c.c.) by means of sodium nitrite (1·3 g. in 15 c.c. of water) was heated on the steam-bath until nitrogen ceased to be evolved. The oil produced, which solidified on cooling, was boiled in dilute sodium hydroxide solution for 15 minutes with charcoal. δ-*o*-Hydroxybenzoylvaleric acid, obtained by acidifying the solution with hydrochloric acid, crystallised from petroleum in long, colourless needles, m. p. 94°; von Braun (*loc. cit.*) gives m. p. 94° (Found: C, 65·0; H, 6·3. Calc., C, 64·8; H, 6·3%).

The phenylhydrazone, prepared by warming the acid with an excess of phenylhydrazine for a few minutes and treating the mixture with dilute acetic acid, had, after recrystallisation from aqueous alcohol, the m. p. (173°) recorded by von Braun.

δ-o-*Acetylaminobenzoylvaleric Acid.*—A mixture of δ-*o*-aminobenzoylvaleric acid with twice its weight of acetic anhydride was heated on the steam-bath for an hour, the excess of acetic anhydride removed under reduced pressure, and the residue poured into water. The viscous product was boiled in alcohol with charcoal, and the δ-o-*acetylaminobenzoylvaleric acid* precipitated, after filtration, by the gradual addition of water was recrystallised from aqueous alcohol, separating in colourless plates, m. p. 153° (Found: C, 64·1; H, 6·7. $C_{14}H_{17}O_4N$ requires C, 63·9; H, 6·5%).

A solution of δ-*o*-acetylaminobenzoylvaleric acid (2 g.) and potassium hydroxide (5·5 g.) in water (35 c.c.) was heated for an hour on the steam-bath, cooled, acidified with hydrochloric acid, and the small colourless precipitate removed. The filtrate yielded δ-*o*-aminobenzoylvaleric acid on successive treatment with potassium hydroxide and acetic acid. The small precipitate was recrystallised from alcohol, when γ-4-*hydroxy*-2-*methylquinoline*-3-*butyric acid* was obtained in colourless prisms, m. p. 241° (Found: N, 5·7. $C_{14}H_{15}O_3N$ requires N, 5·7%).

δ-o-*Formylaminobenzoylvaleric Acid.*—δ-*o*-Aminobenzoylvaleric acid (3 g.) was heated with formic acid (6 g.) on the steam-bath for 3 hours under reflux, the excess of formic acid was then allowed to escape, and the residue yielded a colourless solid on rubbing with alcohol. The product was recrystallised from alcohol and δ-o-*formylaminobenzoylvaleric acid* separated in colourless plates, m. p. 160° (Found: N, 5·5. $C_{13}H_{15}O_4N$ requires N, 5·6%).

One of us (S. G. P. P.) wishes gratefully to acknowledge the receipt of a grant from the Chemical Society Research Fund which has defrayed a part of the cost of this investigation.

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OXFORD. [*Received, June 13th,* 1925.]

CCXXXIX.—*Bismuth Dihydride.*

By EDWARD JOSEPH WEEKS and JOHN GERALD FREDERICK DRUCE.

HAVING prepared solid hydrides of arsenic (*Chem. News*, 1924, **129**, 31) and antimony (this vol., p. 1069), we turned our attention to the analogous solid bismuth dihydride. The method of preparation was similar to one employed in the case of antimony dihydride. A solution of bismuth chloride in hydrochloric acid was added gradually to a mixture of zinc (free from iron, carbon, and arsenic) and fairly strong hydrochloric acid which was rapidly evolving hydrogen. At each addition of bismuth chloride the evolution of gas slackened and could even be made to stop altogether until the bismuth chloride was converted into a flocculent, grey precipitate: $2BiCl_3+8H=Bi_2H_2+6HCl$. When all the zinc (which was used in excess) had dissolved, the liquid was rapidly filtered in an atmosphere of hydrogen, and the precipitate washed many times, first with hot strong hydrochloric acid, then with hot dilute acid, and finally with water until the wash water was neutral. The residue was drained and dried, first in hydrogen and finally in a vacuum desiccator over concentrated sulphuric acid.

On heating in a vacuum, bismuth dihydride gave off hydrogen and left metallic bismuth—quite different from the amorphous dihydride. 0·9184 G. gave 44 c.c. H_2, measured at *N.T.P.*, and 0·9144 g. Bi: H, 0·45; Bi, 99·57. 1·4606 G. lost 0·0088 g. H_2: Bi, 99·39; H, 0·60. On combustion 0·4849 g. gave 0·0235 g. H_2O: H, 0·54 (Bi_2H_2 requires Bi, 99·52; H, 0·48%).

The volume of hydrogen produced was determined as follows: The apparatus, with a quicklime tower in series, was twice filled with nitrogen (previously passed over red-hot copper) and exhausted as completely as possible. The pressure (p) was noted, and the dihydride heated until there was no further pressure change. The final pressure (P) was noted, the apparatus re-exhausted until the pressure was p, and nitrogen, measured at atmospheric pressure, added until the pressure P was restored.

Bismuth dihydride, heated in a tube in absence of air, gave a mirror of bismuth just beyond the heated zone. It thus appeared that the dihydride might decompose into bismuth and bismuthine:

$3Bi_2H_2=2BiH_3+4Bi$. (On heating, cuprous hydride decomposes into copper and cupric hydride [Barlett and Merrill, *Amer. Chem. J.*, 1896, **17**, 185], and arsenic dihydride into arsenic and arsine [Moser and Brukl, *Monatsh.*, 1924, **45**, 25]). To test this supposition, bismuth dihydride was heated in a stream of purified hydrogen. The issuing gas produced in silver nitrate solution a grey precipitate soluble in nitric acid. This was presumably silver bismuthide, as its nitric acid solution, after removal of silver as chloride, gave with hydrogen sulphide a dark brown precipitate, the solution of which in warm dilute nitric acid deposited bismuth hydroxide on addition of ammonia.

Bismuth dihydride prepared as described above was free from zinc, carbon, and iron, but contained a trace of chlorine (less than 0·02%, estimated by Volhard's method).

Fused potassium nitrate reacted very vigorously with the dihydride (as with antimony dihydride), but only slowly oxidised finely divided bismuth.

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[*Received, June 17th*, 1925.]

CCXL.—*The Nature of the Alternating Effect in Carbon Chains. Part III. A Comparative Study of the Directive Efficiencies of Oxygen and Nitrogen Atoms in Aromatic Substitution.*

By ERIC LEIGHTON HOLMES and CHRISTOPHER KELK INGOLD.

THAT directive action in aromatic substitution is the result of an alternating effect transmitted throughout the ring from a key-atom is generally agreed, and a convincing confirmation has recently been given by Pyman and Stanley (J., 1924, **125**, 2484; compare *Ann. Report*, 1924, pp. 110—111). It is the authors' hope to elucidate more precisely the nature of the alternation, and to discover, by the close study of different key-atoms, what property of them it is that is so effectively propagated.

In Part I (this vol., p. 513) it was stated (and this is the starting point of the present investigation) that whilst Kermack and Robinson's hypothesis of an induced electropolar effect requires that oxygen, owing to the greater pre-formation of its octet, should predominate over nitrogen as a negative key-atom,* the theory of alternating free and bound affinity demands that the more unsaturated element, tervalent nitrogen, should have greater influence.

* For references see Part I.

From this theoretical distinction there followed a difference in the predicted orienting effect of the nitroso-group, which was determined, and found to be in agreement with the affinity theory. It was then suggested, however (compare Part II, this vol., p. 870),

(1) that a group with two competing negative atoms constituted a case too complicated for prediction by the polarity principle * (Lapworth),

(2) that the observed facts could be accommodated by means of a different point of view when the atom united to the ring contained a " lone pair " of electrons (Robinson).

A group was therefore examined which (*a*) contained only one negative atom, oxygen, (*b*) was joined to the benzene ring through carbon; and again results were obtained indicating that directive action depends on the unsaturation rather than the polar character of the atom producing it. Since these results were communicated, however, a further suggestion has been made (Robinson, *Chem. and Ind.*, 1925, **44**, 260) which fundamentally affects much of the work in progress. It is

(3) that atoms, previously regarded as negative, such as the oxygen atoms of ethers, may, upon occasion, act as *positive* key-atoms by functioning as " onium " elements.†

Such an occurrence would obviously reverse all the effects to be expected on the basis of the polarity theory, which could thus, in a given case, be reconciled with results otherwise opposed to it.

A series of experiments has therefore been instituted which, while still adhering to conditions (*a*) and (*b*) imposed by the earlier arguments of Lapworth and Robinson (1) and (2), in addition exercises a definite control over the suggestion that " onium " action may account for the exceptions to the polar hypothesis.‡

In order to understand the method employed it is necessary to consider the position of toluene and its monosubstituted products with regard to the principles both of alternating affinity and of alternate polarities.

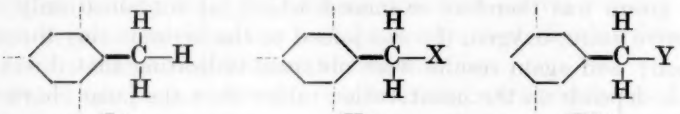
It is fundamental to the affinity theory (compare Flürscheim, *J. pr. Chem.*, 1907, **76**, 197; *Chem. and Ind.*, 1925, **44**, 249) that carbon exerts valencies of more, or less, than the normal affinity content only when compelled to do so by the varying requirements of an unsaturated, or over-saturated, attached atom or group

* That of 1920 was referred to.

† For example, by forming salts with the reagent employed.

‡ Yet another argument (4), recently advanced by Lapworth, is alluded to below (p. 1808).

(mechanism of propagation). In toluene, the phenyl group is unsaturated (possesses residual affinity), and hence the methyl carbon atom is strongly bound, a condition leading to *op*-substitution (I). If, now, one of the methyl hydrogen atoms is replaced by a feebly unsaturated atom (X), the demand made by this atom on the affinity of the carbon atom may be insufficient to counterbalance the unsaturation of the phenyl group, and again *op*-substitution will be the rule (II). On the other hand, if, in place of X, a strongly unsaturated atom (Y) be introduced, then the unsaturation of the phenyl group may be overcome, when a condition will arise leading to *m*-substitution (III):



(I.) (II.) (III.)

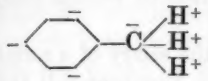
Now bivalent oxygen is a feebly unsaturated atom, whilst tervalent nitrogen is strongly unsaturated. Hence, if we consider comparatively benzyl alcohols (IV) and benzylamines (V) (using these terms in a general sense to include alkyl and acyl derivatives, etc.), the former should be more closely represented by condition (II), and the latter by condition (III):

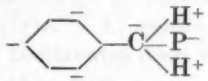
(IV.) $C_6H_5—CH_2—OA$ $C_6H_5—CH_2—NAA'$ (V.)

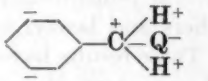
That is to say, the benzylamines should show a greater tendency than the benzyl alcohols towards *m*-direction, as against *op*-direction. Of course, if oxonium or ammonium salt-formation were to take place *op*-direction might result, but, whilst benzyl alcohols should exhibit *op*-direction *in any event*, benzylamines should show *m*-direction if and when salt formation does not occur. *It is still true, therefore, that according to the affinity theory derivatives of benzylamine should show a greater tendency towards* m-*substitution, and a smaller tendency towards* op-*substitution, than the benzyl alcohols, and that* m-*directive action should never prevail amongst the latter.*

On the other hand, according to polarity principles, hydrogen is feebly key-positive (Lapworth, *Mem. Manchester Phil. Soc.*, 1920, **64**, No. 3, p. 5); thus, the *op*-substitution of toluene may be explained (VI). If, now, in place of one of the methyl hydrogen atoms a weakly negative atom (P) be introduced, this may conceivably be insufficient to counterbalance the effect of the two remaining hydrogen atoms, and, in this case, *op*-substitution will still prevail (VII). If, however, a strongly negative atom (Q) is

introduced, the influence of the hydrogen atoms should be overcome and *m*-direction should ensue (VIII).


(VI.)


(VII.)


(VIII.)

Now, if the oxygen atom in benzyl alcohols acts as a negative key-atom, it must be assumed to be like "P" rather than like "Q," for benzyl alcohol derivatives display *op*-substitution (see below). It follows, however, from the electronic principles alluded to at the commencement that if *oxygen* is not negative enough effectively to control substitution from the position it occupies in the benzyl alcohols, then, *a fortiori*, more feebly negative *nitrogen* in the same position will be unable to do so. Assuming, then, that we have to do with *negative* key-atoms in both cases, there should be a greater tendency to *op*-substitution, and a smaller tendency to *m*-substitution, amongst benzylamines than amongst benzyl alcohols.

Let it now be supposed that these elements act in their "onium" forms, that is, as *positive* key-atoms. This would supply a convenient explanation of *op*-substitution in benzyl alcohols, since the methyl carbon atom would now be attached to three positive atoms as in toluene. But the same principles which require that oxygen shall be more effective than nitrogen as a negative key-atom also demand that nitrogen shall be more powerful when both are positive (Robinson, *loc. cit.*). Hence, in this case also, benzylamines should show the greater tendency to *op*-substitution.

The only remaining case is that which would arise if, under the condition of substitution, oxonium salts could not be formed, whilst the more stable, analogous, ammonium salts could; oxygen would then be a negative key-atom, but nitrogen might be a positive one. Obviously, however, the expected differences would, in this case, *still* be in the sense previously stated, only greater. *Thus, in all three cases, polarity principles require that benzylamines shall show a greater tendency to* op-*substitution, and a smaller tendency to* m-*substitution, than benzyl alcohols.*

It follows, then, that in the comparison of benzyl alcohols with benzylamines we have a clear issue, from which the theory of "onium-action" provides no exit.

Before the commencement of this investigation several observations had already been made indicating the prevalence of *op*-substitution in benzyl alcohol derivatives of the type $C_6H_5 \cdot CH_2 \cdot O \cdot A$. Thus Beilstein and Kühlberg (*Annalen*, 1868, **147**, 341) obtained

p-nitrobenzyl acetate by direct nitration of benzyl acetate (A = ·CO·CH_3), whilst Staedel (*Annalen*, 1883, **217**, 177) prepared several *p*-nitrobenzyl derivatives by the nitration of benzyl phenyl ethers and benzyl tolyl ethers (A = Aryl).

These results have now been generalised by the study of a number of new cases, chosen in such a way as to give oxonium salt formation, if it occurs, the greatest possible opportunity to manifest its effects.

As is well known, the stability of ammonium salts (and, it may be assumed, of "onium" salts in general) is diminished by the introduction of an acyl group in the place of an alkyl group (compare the basicity of acetanilide with that of methylaniline); and the greater the strength of the acid from which the acyl group is derived, the more completely is the salt formation suppressed. It might therefore be supposed that even if oxonium salt formation, resulting in "positive" oxygen, is the cause of the *op*-substitution of benzyl ethers (A = Alkyl), the tendency to this type of substitution would become less marked in benzyl esters of weak acids (*e.g.*, benzyl acetate; A = ·CO·CH_3), and non-existent in benzyl esters of strong mineral acids (*e.g.*, benzyl nitrate; A = ·NO_2), since an anhydro-union with strong mineral acids, like nitric acid and sulphuric acid, is known to suppress the ammonium salt formation of even comparatively strong nitrogen bases.

Cases have therefore been selected in such a way as to furnish examples of all these three classes; and in every case it has been found that substitution occurs mainly or exclusively in the para-position; *m*-substitution has in no instance been observed, despite the variation in the character of "A."

The examples on which the above general statement is based are collected together in the following table. They afford, it is believed, strong grounds for the conclusions (a) *that* op-*substitution prevails amongst benzyl alcohol derivatives of the type* C_6H_5–CH_2–OA, *whether A = alkyl or acyl;* (b) *that oxonium salt formation with the reagent employed is not the cause of this phenomenon.*

TABLE I.

C_6H_5–CH_2–OA (class).	A·OH.	Result.	Reference.
A = alkyl	*s*-Tribromophenol	*p*	This paper.
	mm-Dinitro-*p*-cresol	*p*	Staedel (*loc. cit.*).*
A = acyl (A·OH = weak acid)	Acetic acid	*p*	Beilstein and Kühlberg (*loc. cit.*).
A = acyl (A·OH = strong acid)	Picric acid	*p*	This paper.
	Nitric acid	*p*	,, ,,

* Staedel also nitrated the ethers in which A = phenyl, *o*-tolyl, and *p*-tolyl. In each of these cases nitro-groups entered both rings, but that which entered the benzyl group did so in the *p*-position.

In the case of the benzylamines the only compounds of the type $C_6H_5 \cdot CH_2 \cdot NAA'$ which have been examined (so far as we have ascertained) in regard to ring substitution prior to this investigation are (i) acetobenzylamide (A = H; A′ = ·CO·CH$_3$) and (2) phenylethylbenzylamine (A = Et; A′ = Ph). Acetobenzylamide was found by Amsel and Hofmann to nitrate in the *p*-position (*Ber.*, 1886, **19**, 1286), a result which we have confirmed. Phenylethylbenzylamine was stated by Schultz and Bosch (*Ber.*, 1902, **35**, 1292) to nitrate in the *m*-position in the benzyl group; but doubt has been cast on this result (Flürscheim, *Chem. and Ind.*, 1925, **44**, 285), a doubt which is increased by the investigation recorded in this paper of the closely analogous case of methyldibenzylamine (A = Me; A′ = CH_2Ph).* It was apparent at the outset, therefore, that no general conclusion with regard to the substitution of benzylamine could be reached on the basis of previously recorded observations, and that before the comparison with benzyl alcohols could be made a series of experiments on representative benzylamines was necessary.

Such a series has now been carried out, and, in contrast to the results obtained with the benzyl alcohols $C_6H_5 \cdot CH_2 \cdot OA$, it has been found that predominant *m*-substitution is of common occurrence amongst derivatives of benzylamine, $C_6H_5 \cdot CH_2 \cdot NAA'$.

As in the previously described experiments, examples were selected in such a way as to obtain a maximum of control over effects due to ammonium salt formation.

The effects to be expected from this cause may be inferred from the case of aniline. As Bamberger has shown (*Ber.*, 1895, **28**, 399), aniline nitrate, $C_6H_5 \cdot NH_3 \cdot O \cdot NO_2$, which is *m*-orienting, readily loses water under ordinary nitration conditions, giving the nitroamine $C_6H_5 \cdot NH \cdot NO_2$, which, being insufficiently basic to form a stable salt, substitutes in the *op*-positions; hence arise the different results obtained with different concentrations of nitric acid. Now according to the theory of alternating free and bound affinity the nitrogen atom in benzylamine should direct oppositely to that in aniline when both are in analogous states of combination. Hence it might be expected that under ordinary conditions (concentrated nitric acid in the cold) the conversion of the nitrate $C_7H_7 \cdot NH_3 \cdot O \cdot NO_2$ into a non-basic nitroamine, $C_7H_7 \cdot NH \cdot NO_2$, would determine predominant substitution in the *m*-position. Actually this is what occurs, and, apart from analogy with aniline, there are four inde-

* We have not, however, repeated the experiments of Schultz and Bosch, since Prof. Robinson has recently announced his intention of doing so (*Chem. and Ind.*, 1925, **44**, 227).

pendent experimental reasons for concluding that it takes place in the manner suggested.

First, under the conditions stated, the *m*-nitro-derivative, although the main product (about 80%), is not the only one; a certain quantity of *p*-isomeride is also formed, and (possibly) a trace of ortho. If the explanation given is correct, this must mean that, at the temperature employed (0° to 20°), only a part of the benzylamine nitrate is dehydrated to benzylnitroamine. But an increase of temperature would easily complete this reaction and should thus suppress the by-products of the nitration. This was found to be the case: on nitration at temperatures approaching 100° the *m*-nitro-compound was obtained as sole product and in practically quantitative yield.*

Secondly, it follows from the explanation given that the phenomena observed with benzylamine should be reproduced in secondary benzylamines, $C_7H_7{\cdot}NHAlk$, but should disappear in tertiary derivatives, $C_7H_7{\cdot}N(Alk)_2$, since these lack the amino-hydrogen atom necessary for dehydration of the salt to the nitroamine. This was also observed, exactly as predicted: methylbenzylamine, $C_7H_7{\cdot}NH{\cdot}CH_3$, and dibenzylamine, $C_7H_7{\cdot}NH{\cdot}C_7H_7$, behave like benzylamine, directing mainly or exclusively towards the *m*-position, according to temperature; methyldibenzylamine, however, $(C_7H_7)_2NMe$, showed no tendency towards *m*-direction, but, on the contrary, gave *op*-products.

Thirdly, since the introduction of one acyl group into a primary amine greatly increases the difficulty of replacing the second amino-hydrogen atom by another acyl group, the prior mono-acylation of a benzylamine should prevent the formation under nitration conditions of a nitroamine, excepting, perhaps, at high temperatures. Now benzylamines are strong bases, and hence, if the acyl group introduced is derived from a weak acid, the substituted amide should be definitely basic, and it is true that acetobenzylamide, acetodibenzylamide, and acetomethylbenzylamide form moderately stable salts with mineral acids. Substitution in these compounds should therefore take place mainly, if not exclusively, through their salts, that is, in the *op*-positions. Further, since acetodibenzyl-

* This temperature effect may be contrasted with that observed in the sulphonation of aniline, which gives *m*-sulphanilic acid in the cold (substitution of sulphate) but *p*-sulphanilic acid at higher temperatures (the sulphate passing into the sulphamic acid under these conditions). Thus an increase of temperature causes a *p*-product to appear in the place of *m*-, in the case of aniline, but a *m*-product in the place of *p*-, when the directing nitrogen atom is one place further from the nucleus, as in benzylamine—a clear illustration, similar in some respects to that given by Pyman and Stanley (*loc. cit.*), of the essentially *alternating* character of the effect transmitted.

amide, $(C_7H_7)_2NAc$, is a definitely weaker base than methyldibenzylamine, $(C_7H_7)_2NMe$, larger quantities of *m*-by-products should be produced in the former case than in the latter. Again, since acetobenzylamide and acetomethylbenzylamide are stronger bases than acetodibenzylamide, the last should yield the largest quantity of *m*-compound. Again, in the case of the very feebly basic acetodibenzylamide, the addition of different quantities of water to the nitric acid used in the nitration should, by altering the degree of hydrolysis of the salt, change the proportion of by-products: the more dilute the acid, the greater should be the proportion of *m*-product obtained. All these predictions have been verified in every detail.

Fourthly, diacetylbenzylamine, $C_7H_7{\cdot}N(CO{\cdot}CH_3)_2$, is non-basic, and it obviously cannot form a nitroamine; it must therefore nitrate as such. It follows that if *m*-substitution in benzylamine derivatives depends essentially on tervalent nitrogen, then this diacetyl compound, unlike the monoacetyl derivatives previously mentioned, should undergo substitution wholly or mainly in the *m*-position. This was found to be the case.

These results, which are summarised in the following table, give strong grounds * for the conclusion that *not only is* m-*substitution a frequent experience with benzylamine derivatives,*

$$C_6H_5{\cdot}CH_2{\cdot}NAA',$$

but that it prevails in every case in which substitution through a salt is precluded.

TABLE II.

Substance.	Main product.	By-product.	Reference.
Benzylamine	*m*	*p*†	This paper.
Methylbenzylamine	*m*	*p*†	,, ,,
Dibenzylamine	*m*	*p*†	,, ,,
Methyldibenzylamine	*p* (*o*)	—	,, ,,
Acetobenzylamide	*p*	*m*?	Amsel and Hofmann (*loc. cit.*).
Acetomethylbenzylamide...	*p*	*m*?	This paper.
Acetodibenzylamide	*p* (*o*)	*m*	,, ,,
Diacetylbenzylamine	*m*	—	,, ,,

† Only perceptible at low temperatures.

Comparing now the benzyl alcohols and benzylamines, we see that, as the affinity theory demands, compounds of the former class belong exclusively to the *op*-directing series, whilst those of the latter display a strong tendency to *m*-substitution. Polarity

* For the sake of maintaining the strict comparison with benzyl alcohol derivatives, no use is here made of the few known instances of ring-substitution in benzylamines already substituted in the benzyl group, although the data are consistent with the results now described.

principles, as shown above, require a difference of precisely the opposite kind.

In Part II * (*loc. cit.*) a peculiarly substituted benzyl ether was examined in which the two side-chain hydrogen atoms of the ordinary benzyl group were removed from possible competition with the oxygen atom by replacing them by a doubly-bound methylene group, $:CH_2$. The compound was α-methoxystyrene,

$$C_6H_5{\cdot}C(OMe){:}CH_2,$$

and some importance was attached to the case because it indicated in a particularly clear manner that *unsaturation*, rather than negative character, is the cause of directive action. Recently, however, a new suggestion, additional to those mentioned above (1, 2, and 3, p. 1801), has been advanced. It is

> (4) that the unsaturated group, C:C, *itself* might behave as a " negative " key-group in the sense of the polarity rule, and hence in methoxystyrene act as would an oxygen atom directly attached to the benzene nucleus (Lapworth, *Chem. and Ind.*, 1925, **44**, 228, 398).

We express no opinion as to the *a priori* probability of this suggestion, but wish to point out that it (like every argument † which has been advanced in defence of the polarity theory since these investigations were commenced) has been taken into serious account in devising the experiments now described. It is completely answered. For if the *op*-direction of methoxystyrene is due to the " negative " double bond, why does it persist, against the polar principles cited above, when that double bond is absent, as in the benzyl ethers, $C_6H_5{\cdot}CH_2{\cdot}OA$? The cause lies not in the two hydrogen atoms (pp. 1802—1803, 1807, 1808), nor in a " positive " oxygen atom (pp. 1804—1805, 1807), nor in the group A (pp. 1804—1805, 1805—1807); for if it did, the *m*-direction of analogous benzylamines could not be explained. The same difficulty confronts any attempt to base an explanation, or argument,‡ on the " damping

* On p. 871, lines 11–12, " two intrinsically negative atoms in competition for the function of key-atom " should be read in place of " two competing negative key-atoms," since the ellipsis used has caused misunderstanding.

† General arguments, such as the imputation of " insisting that any atom you like to choose must be a key-atom " (Robinson, *Chem. and Ind.*, 1925, **44**, 227), we regard as not justified in view of the full reasons that have invariably been given for each assumption made. Arguments of this kind are excepted from the statement to which this footnote refers.

‡ The relevance to the polarity theory of the cases under discussion was admitted by Robinson when predicting, on the basis of his theory, the position of substitution of the benzylamine examined by Schultz and Bosch (p. 1805); which should obviously yield *op*-substitution derivatives according to *any* of the theories discussed in this paper.

action " of the saturated carbon atom (Robinson, *Chem. and Ind.*, 1925, **44**, 148; Lapworth, *ibid.*, p. 398), or on lack of " conjugation " of the key-atom with the nucleus.

It seems to us that there is only one *consistent* explanation of these facts, namely, that which has uniformly and correctly foretold events throughout this series of investigations. Proof has been given that the efficiencies of " negative " key-atoms stand, not in the order of their electron affinities, but in the order of their unsaturation; and it seems fair, therefore, to conclude that unsaturation is the property transmitted. This is the essence of Flürscheim's form of the alternating theory. We are aware that by identifying unsaturation with potentially mobile electrons, and its alternating distribution with a similarly propagated electronic displacement, a nearly equivalent theory may be formulated * (compare Robinson, *Chem. and Ind.*, 1924, **43**, 1297; 1925, **44**, 118; this vol., p. 370). But this cannot add validity to the fundamental idea, nor can it inspire enhanced confidence whilst the interpretation of the chemical terms remains speculative. We suggest, therefore, without denying the possibility of polar alternation, that the facts thus far adduced constitute grounds for the conclusion that the propagation of alternating unsaturation is the prime directive process in ordinary aromatic substitution.

Experimental.

(*A*) *Nitration of Benzyl Ethers and Esters.*

(i) s-*Tribromophenyl Benzyl Ether*, $C_6H_2Br_3\cdot O\cdot CH_2Ph$.—Equimolecular quantities of benzyl chloride and *s*-tribromophenol were added to a suspension of sodium ethoxide in boiling toluene, the filtered solution was evaporated, and the residue recrystallised from alcohol. The product, m. p. 86—87°, had the properties described by Auwers (*Annalen*, 1907, **357**, 92).

For the nitration, the ether was added in small quantities to concentrated nitric acid at about — 5°, the solution kept for 1 hour, poured on to ice, and the solid obtained, after draining from a small quantity of adhering oil, crystallised from alcohol, when it separated in small prisms, m. p. 145° (Found : N, 3·1. $C_{13}H_8O_3NBr_3$ requires N, 3·0%). An impure by-product was obtained of higher nitrogen content.

s-*Tribromophenyl* p-*nitrobenzyl ether*, $C_6H_2Br_3\cdot O\cdot CH_2\cdot C_6H_4\cdot NO_2$, with which the above substance was identified, was prepared for comparison by the interaction of *p*-nitrobenzyl chloride and sodium *s*-tribromophenoxide in benzene solution. It separated in a moder-

* It involves, however, a reversal of postulated key-atom efficiencies.

ately pure form when ligroin was added to the filtered and evaporated liquid.

(ii) op-*Dinitrophenyl Benzyl Ether*, $C_6H_3(NO_2)_2 \cdot O \cdot CH_2Ph$.—This compound, which was prepared by Kumpf's method (*Annalen*, 1884, **224**, 131), was nitrated under the conditions used in the previous experiment; on addition of ice a precipitate was obtained which, twice crystallised from benzene, gave well-defined, orange-yellow needles, m. p. 198°, of *op*-dinitrophenyl *p*-nitrobenzyl ether (Staedel, *loc. cit.*; Kumpf, *loc. cit.*). The latter method, using, however, *p*-nitrobenzyl chloride in place of the iodide, and heating in the absence of a solvent at 150°, was employed in order to obtain a specimen for comparison.

(iii) *Benzyl Nitrate*, $C_6H_5 \cdot CH_2 \cdot O \cdot NO_2$.—Prepared from benzyl chloride and silver nitrate by Nef's method (*Annalen*, 1889, **309**, 171), and isolated and purified by distillation in a vacuum, this substance, which, after twice distilling, had b. p. 101—105°, was analytically pure, and free from halogen, was run during about 4 hours through a fine capillary tube into seven times its weight of 95% nitric acid at about −10°, and the solution immediately poured on to ice. The oil thus precipitated slowly solidified, and the solid, which was drained on porous porcelain and crystallised from warm aqueous alcohol, was identified as *p*-nitrobenzyl nitrate by its m. p. (71°) and by direct comparison with a specimen prepared by Nef's method from *p*-nitrobenzyl chloride and silver nitrate. On oxidation with 3% alkaline permanganate solution (equiv. to rather more than 2O) at about 100°, *p*-nitrobenzoic acid was obtained.

A considerable amount of oxidation took place during attempts to nitrate benzyl ethyl ether, and even more in the case of benzyl alcohol. The attempts were therefore abandoned.

(B) *Nitration of Primary, Secondary, and Tertiary Benzylamines and of certain Mono- and Di-acetyl Derivatives.*

(iv) *Benzylamine.*—This was prepared from potassium phthalimide and benzyl chloride by Gabriel's method (*Ber.*, 1887, **20**, 2227), but the tedious process of hydrolysing the phthalobenzylimide with hydrochloric acid in sealed tubes was replaced by the following two-stage method, which is conveniently carried out with larger quantities of material. The phthalobenzylimide is boiled for ½ hour with half its weight of potassium hydroxide in 10% aqueous solution. The *phthalobenzylamic acid*,

$$CH_2Ph \cdot NH \cdot CO \cdot C_6H_4 \cdot CO_2H,$$

produced on acidification crystallises from alcohol in slender needles, m. p. 155° (Found: C, 70·0; H, 5·1. $C_{15}H_{13}O_3N$ requires C, 70·3; N, 5·1%).

The crude amic acid was boiled for 18 hours with 20% hydrochloric acid (3 parts), the phthalic acid removed from the cooled solution, and the filtrate evaporated to dryness. The benzylamine isolated from the residue of hydrochloride by means of ether and sodium hydroxide was purified by distillation.

Another method, also a convenient one for the preparation of large quantities, consists in warming in chloroform solution a mixture of equal weights of hexamethylenetetramine and benzyl chloride, and hydrolysing the product with a mixture of concentrated hydrochloric acid and 95% alcohol (1 : 3 by volume).

Nitration of Benzylamine at Different Temperatures.—The general results of the experiments on the nitration of benzylamine at temperatures ranging from −10° to 105° have already been described. The experiments were all carried out, so far as possible, under comparable conditions as to strength and amount of nitric acid. Details of two illustrative cases are given below.

(*a*) Benzylamine (2 g.) was run through a capillary tube during 2 hours into 10 c.c. of 95% nitric acid cooled to −10°. After remaining for 1 hour at this temperature, the product was mixed with ice. The crystals (1·4 g.) which separated during the next few hours consisted of almost pure *m*-nitrobenzylamine nitrate, m. p. 210° (the correct m. p. being 214°; see below). The filtrate was made alkaline with sodium hydroxide and extracted with ether, the extract shaken with a small excess of 2*N*-nitric acid, and the aqueous solution of nitrates evaporated. From the mixture thus obtained a further quantity of *m*-nitrobenzylamine nitrate was readily isolated by fractional crystallisation. The *p*-isomeride, which was also present, could not be fully purified, however, and the more soluble nitrates were therefore converted into the free bases, and these were acetylated with acetic anhydride in the usual manner. Crystallisation from water readily gave the pure acetyl derivative of *p*-nitrobenzylamine. The presence of an *ortho*-compound in the ultimate residues of this and similar experiments was suspected, but could not be definitely established owing to the smallness of the quantity.

(*b*) Benzylamine was added quickly to nitric acid at 100° and the product worked up in the manner just described. The yield of *m*-nitrobenzylamine nitrate was practically quantitative; no trace of the *p*- or *o*-compound could be detected.

o-, *m*-, and *p*-Nitrobenzylamines, which have not been previously described, were prepared by methods which determined their constitution.

o-*Nitrobenzylamine.*—A mixture of *o*-nitrobenzyl chloride (5 g.)

with 10% alcoholic ammonia (50 c.c.) was shaken for 2 hours and kept until the deposition of solid matter ceased (1—2 weeks). The solution was filtered and evaporated, and the residue, which was partly solid and partly liquid, lixiviated with water, in which the solid portion dissolved. On evaporation of this aqueous solution to dryness a well-crystallised hydrochloride was obtained, from which o-*nitrobenzylamine*, a colourous oil, was extracted with ether after the addition of sodium hydroxide. The base could not be induced to crystallise and was therefore characterised by means of its salts and acetyl derivative.

The *hydrochloride* separated from water in colourless needles, m. p. 248° (Found: Cl, 18·6. $C_7H_9O_2N_2Cl$ requires Cl, 18·8%), and the *nitrate* from the same solvent in small, white prisms, m. p. 173—174° (decomp.).

m-*Nitrobenzylamine*.—This was prepared from *m*-nitrobenzyl chloride by the same method and was obtained as a colourless oil which refused to crystallise.

The *hydrochloride* crystallised from water in large, colourless leaflets, m. p. 250°; and the *nitrate* in colourless, flattened needles, m. p. 214° (decomp.) (Found: C, 39·1; H, 4·2. $C_7H_9O_5N_3$ requires C, 39·1; H, 4·3%).

p-*Nitrobenzylamine*.—This was prepared in a like manner from *p*-nitrobenzyl chloride, but could not be induced to solidify. It was identified by means of its known acetyl derivative, a specimen of this being prepared for comparison by the method of Amsel and Hofmann (*loc. cit.*). The free base was further characterised by its *hydrochloride*, which separated from ethyl alcohol in colourless, flattened needles, m. p. 224° (Found: Cl, 18·9. $C_7H_9O_2N_2Cl$ requires Cl, 18·8%); and its *nitrate* crystallised from water in yellow plates, m. p. 180—181°.

(v) *Methylbenzylamine*, $C_6H_5{\cdot}CH_2{\cdot}NHMe$.—The preparation of this substance in quantity by methods given in the literature presented initial difficulties, but two satisfactory methods were ultimately obtained, one a modification of Hinsberg's process, and the other depending on the regulated interaction of benzyl chloride with methylamine.

(*a*) p-*Toluenesulphonbenzylamide*, $CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}CH_2Ph$.—Benzylamine (20 g.) was dissolved in dry pyridine and 40 g. of *p*-toluenesulphonyl chloride were added cautiously and with shaking. The mixture, which became hot and of a deep red colour, was kept for 1 hour and then poured into water. The oily precipitate, which solidified on rubbing, was crystallised from alcohol, when long, stout, colourless prisms, m. p. 114°, were obtained (Found: N, 5·2. $C_{14}H_{15}O_2NS$ requires N, 5·37%).

p-*Toluenesulphonbenzylmethylamide*, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NMe \cdot CH_2Ph$.—The above amide (40 g.), methyl iodide (80 g.), alcohol (20 c.c.), and aqueous sodium hydroxide were shaken together for about an hour, the sodium hydroxide being kept in sufficient excess to render the mixture strongly alkaline throughout the period. The mixture was heated on the steam-bath for 15 minutes and poured into water, and the oily precipitate, which solidified, was crystallised from alcohol, from which the pure benzylmethylamide separated in colourless plates, m. p. 95° (Found: N, 5·4. $C_{15}H_{17}O_2NS$ requires N, 5·1%).

Some difficulty was experienced in hydrolysing this substance, the convenient general process of warming with a mixture of acetic and sulphuric acids failing owing to the instability of the product under the conditions. Hydrolysis was, however, effected by heating the amide for 7 hours at 165—170° with 1·5 times its weight of concentrated hydrochloric acid. (Below 155°, the hydrolysis is extremely slow, whilst above 175° an extensive separation of carbon takes place.) The base was extracted with ether from the cooled, basified solution, and separated from neutral impurities by re-extraction with aqueous hydrochloric acid. It was finally recovered from the crystallised hydrochloride by extraction with ether in the presence of alkali, and purified by distillation.

(*b*) A mixture of benzyl chloride (20 g.), alcohol (200 c.c. of 95%), and aqueous methylamine (70 c.c. of 33% solution) was heated in a well-stoppered flask at 60° for an hour and allowed to cool. The alcohol was removed by distillation, the residue made alkaline and extracted with ether, and the extract dried with potassium carbonate and evaporated. The residue thus obtained, on distillation, yielded a large fraction, b. p. 180—200°, which on redistillation boiled almost completely at 184—186°, consisting of pure methylbenzylamine. The fraction boiling above 200° was heated with an excess of acetic anhydride for a few minutes, and then with water. The solution, after being made alkaline, was extracted with ether, and the extract washed with very dilute hydrochloric acid and then evaporated. The residue, on boiling for 12 hours with 20% hydrochloric acid, yielded a further quantity of methylbenzylamine hydrochloride, which was decomposed to give the free base.

The base prepared by any of these methods had b. p. 184—186°, and was characterised by means of its *hydrochloride*, which separated from ethyl alcohol in rosettes of needles, m. p. 195° (Found: Cl, 22·4. $C_8H_{12}NCl$ requires Cl, 22·5%).

Nitration of Methylbenzylamine at Different Temperatures.—Nitration at low temperature was conducted much as described for

the case of benzylamine, but no precipitation was obtained on the addition of ice. The product was therefore made strongly alkaline and extracted with ether, and the combined ethereal extracts were shaken several times with dilute hydrochloric acid. On evaporation of the acid solution crystals were not obtained until the whole of the solvent had been removed, when a solid remained, which was recrystallised from ethyl alcohol. In this way a small quantity of a moderately soluble salt was easily separated from the large amount of a very soluble salt which accompanied it. The somewhat sparingly soluble salt, after twice crystallising, separated in colourless, flattened needles, m. p. 226°, which did not depress the m. p. of an authentic specimen (see below) of methyl-*p*-nitrobenzylamine hydrochloride. The readily soluble salt separated sometimes as laminæ and sometimes in rosettes of needles. After thrice crystallising, it melted at 181° and was identified as methyl-*m*-nitrobenzylamine hydrochloride by comparison and by the m. p. of a mixture with a genuine specimen (below). The yields of *p*- and *m*-isomerides were usually about 10% and 80% respectively, about 10% of the material being either lost during manipulation or not separated. Careful search was made for the *o*-compound, but this could not be isolated, and all the impure residues had their m. p.'s depressed by admixture with a specimen of pure methyl-*o*-nitrobenzylamine hydrochloride. When the nitration was conducted at temperatures approaching 100°, no *p*-isomeride was formed, the product consisting wholly of the *m*-nitro-compound.

Methyl-o-*nitrobenzylamine*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NHMe$.—After a mixture of *o*-nitrobenzyl chloride (5 g.), 95% ethyl alcohol (30 c.c.), and 33% aqueous methylamine (30 c.c.) had been kept for a week, the solution was filtered and evaporated and the semi-solid residue mixed with dilute hydrochloric acid and evaporated to dryness. The oily base liberated from this hydrochloride refused to crystallise and was therefore identified through its hydrochloride, which, when crystallised from water, formed small, pale yellow prisms, having the m. p. (175°) and properties recorded by Gabriel and Jansen (*Ber.*, 1891, **24**, 3090).

Methyl-m-*nitrobenzylamine* was prepared from *m*-nitrobenzyl chloride and methylamine as described above, and as it was an oil which would not solidify, was characterised by means of its salts.

The *hydrochloride* separated from alcohol in small, colourless, flattened needles, m. p. 182° (Found: Cl, 17·5. $C_8H_{11}O_2N_2Cl$ requires Cl, 17·4%), and the *nitrate* from dilute nitric acid in long, flattened needles, m. p. 150°.

Methyl-p-*nitrobenzylamine* was also obtained as an oil and char-

acterised by its *hydrochloride*, flattened needles, m. p. 226° (Found: Cl, 17·5. $C_8H_{11}O_2N_2Cl$ requires Cl, 17·4%).

(vi) *Dibenzylamine*, $(C_6H_5{\cdot}CH_2)_2NH$: *Nitration at Different Temperatures.*—As heretofore, a description is given of one experiment carried out at a low temperature and one at a high temperature.

(*a*) Kahlbaum's dibenzylamine (4 g.) was allowed to flow during 4 hours through a capillary tube into 20 c.c. of nitric acid (*d* 1·5) maintained at $-5°$ to 0°. After keeping for a further hour at the same temperature, the product was poured on to ice and the crystalline precipitate collected and crystallised from 800 c.c. of boiling water, when 5·0 g. of pure *mm'*-dinitrodibenzylamine nitrate separated in clusters of needles, m. p. 235° (decomp.). It was identified by analysis and by direct comparison with a genuine specimen (below), and also by converting it into the free base, which was crystallised and similarly identified. The crystals obtained on evaporating the mother-liquors (2 g.) obviously consisted of a mixture, and, by fractional crystallisation from water, and extraction with small amounts of boiling water, were divided into a less soluble salt, identical with that obtained above, and a more soluble salt, which, when pure, had m. p. 210° and was identified as *pp'*-dinitrodibenzylamine nitrate by analysis and by comparison with a specimen obtained as described below. The yields of *pp'*- and *mm'*-dinitro-products isolated were 5% and 80% respectively. A third isomeride appeared to be present, but could not be fully purified; it may have been the *mp'*-compound, as it depressed the m. p. of an authentic specimen of the *oo'*-isomeride on admixture.

(*b*) On adding dibenzylamine rapidly to 10 parts by weight of nitric acid (*d* 1·5) at 70—90°, and pouring the product into water, *mm'*-dinitrodibenzylamine nitrate was obtained in almost theoretical yield. No isomeride could be isolated.

oo'-*Dinitrodibenzylamine*, $(NO_2{\cdot}C_6H_4{\cdot}CH_2)_2NH$.—This substance, prepared by Gabriel and Jansen's method (*loc. cit.*), melted at 101°, and its hydrochloride at 238° (decomp.). Gabriel and Jansen record the m. p. of the base as 99—100° and that of the hydrochloride as "above 220°." Birk gives m. p. 236° for the hydrochloride (*J. pr. Chem.*, 1897, **56**, 360).

The *nitrate* separated from water in pale yellow needles, m. p. 200—203° (decomp.) (Found: C, 47·9; H, 3·9. $C_{14}H_{14}O_7N_4$ requires C, 48·0; H, 4·0%).

mm'-*Dinitrodibenzylamine.*—A solution of *m*-nitrobenzyl chloride in 5 parts of 10% alcoholic ammonia was kept until crystals ceased to form, when they were collected, lixiviated with water to remove ammonium chloride, and crystallised from alcohol or ether, from

which stout, lemon-yellow prisms separated, m. p. 83·5°. A further quantity was obtained from the semi-solid mass remaining on evaporation of the ammoniacal alcoholic solution by alternately extracting with water and crystallising from alcohol (Found: C, 58·6; H, 4·4. $C_{14}H_{13}O_4N_3$ requires C, 58·5; H, 4·5%).

The *hydrochloride*, formed by dissolving the base in hot dilute hydrochloric acid and cooling, crystallised in small, very pale yellow prisms, m. p. 253°; whilst the *nitrate*, prepared similarly, or by nitration as described above, separated in bunches of very pale yellow needles, m. p. 235° (decomp.) (Found: C, 48·2; H, 4·2. $C_{14}H_{14}O_7N_4$ requires C, 48·0; H, 4·0%).

pp′-*Dinitrodibenzylamine*.—This was prepared from *p*-nitrobenzyl chloride and alcoholic ammonia as in the experiment described above. The base separated from alcohol in pale buff needles, m. p. 93° (Found: C, 58·5; H, 4·6%). It is only sparingly soluble in ether (distinction from the *mm′*-compound).

The *hydrochloride* crystallises from hot water in clusters of colourless needles, m. p. 217—218°, and the *nitrate*, prepared either by nitration of dibenzylamine as described above, or by cooling a solution of the dinitro-base in hot dilute nitric acid, forms very pale yellow leaflets, m. p. 210—211° (decomp.) (Found: C, 48·2; H, 4·3. $C_{14}H_{14}O_7N_4$ requires C, 48·0; H, 4·0%).

(vii) *Methyldibenzylamine*, $(C_6H_5\cdot CH_2)_2NMe$.—Benzyl chloride (20 g.) was dissolved in 200 c.c. of ethyl alcohol and mixed with 40 c.c. of 33% aqueous methylamine. The reaction was allowed to proceed in the cold and finished by heating at 60° for a short time. After evaporation of the alcohol the bases were extracted with ether, after the addition of sodium hydroxide, and treated with *p*-toluenesulphonyl chloride as described on p. 1812. On extracting an ethereal solution of the crude product thus obtained with dilute hydrochloric acid a solution of dibenzylamine hydrochloride was obtained; the free base, isolated from this by extraction with ether after the addition of alkali, had b. p. 290° (uncorr.) (Emde, *Arch. Pharm.*, 1909, **247**, 369, records b. p. 304—305°, corr.). The *hydrochloride*, crystallised from a concentrated solution in hydrochloric acid, has m. p. 200—201° (Found: Cl, 14·2. $C_{15}H_{18}NCl$ requires Cl, 14·0%).

The nitration of this substance was carried out both in carefully cooled, and in warm, nitric acid, but substantially the same results were obtained in the two cases, and the following description will suffice as illustration. The base was allowed to flow through a fine capillary tube into seven times its weight of 95% nitric acid at 0°. The product was allowed to warm to the ordinary temperature during 2 hours and was then mixed with ice, when an

oily precipitate was obtained which solidified. This was suspended in aqueous sodium hydroxide and shaken with ether, and the ethereal solution obtained was dried and evaporated, yielding a solid residue consisting mainly of *pp'*-dinitrodibenzylmethylamine. This substance was readily isolated by crystallisation from alcohol and was identified with an authentic specimen prepared as described below. The ultimate residues from these crystallisations were oily, but responded to seeding with a crystal of the pure *oo'*-dinitro-compound, a small amount of which was isolated by draining the adhering oil into porous porcelain and crystallised from ether. It was identified by direct comparison and a mixed m. p. determination.

oo'-*Dinitrodibenzylmethylamine*, $(NO_2 \cdot C_6H_4 \cdot CH_2)_2N \cdot CH_3$.—A mixture of *o*-nitrobenzyl chloride (5 g.), absolute alcohol (30 c.c.), and 33% aqueous methylamine (15 c.c.) was kept at the ordinary temperature for a week. The crystals which had separated were recrystallised from alcohol, when stout, yellow prisms were obtained agreeing in their m. p. (63°) and properties with the description of *oo'*-dinitrodibenzylmethylamine given by Gabriel and Jansen (*loc. cit.*).

The *hydrochloride* crystallised from dilute hydrochloric acid in colourless needles, m. p. 216° (Found: Cl, 10·3. $C_{15}H_{16}O_4N_3Cl$ requires Cl, 10·5%), and the *nitrate* from dilute nitric acid in very pale yellow prisms, m. p. 125° (decomp.).

mm'-*Dinitrodibenzylmethylamine*, prepared in like manner from *m*-nitrobenzyl chloride and methylamine, separated from ethyl alcohol in colourless needles, m. p. 83—84° (Found: C, 59·9; H, 5·1. $C_{15}H_{15}O_4N_3$ requires C, 60·0; H, 5·0%).

The *hydrochloride*, prepared by evaporating a solution of the base in hydrochloric acid and crystallising the residue from alcohol, formed pale buff prisms, m. p. 223—224° (Found: Cl, 10·2. $C_{15}H_{16}O_4N_3Cl$ requires Cl, 10·5%), and the *nitrate*, crystallised from dilute nitric acid, was obtained as small, pale yellow prisms, m. p. 163° (decomp.).

pp'-*Dinitrobenzylmethylamine*.—This was obtained by the same method and had the m. p. and properties recorded by Paal and Sprenger (*Ber.*, 1897, **30**, 63).

The *hydrochloride*, prepared as in the previous case, crystallised from ethyl alcohol in stout, pale yellow prisms, m. p. 204—205° (Found: Cl, 10·4%), whilst the *nitrate*, after twice crystallising from water, formed pale yellow prisms, m. p. 146° (Found: C, 49·3; H, 4·7. $C_{15}H_{16}O_7N_4$ requires C, 49·4; H, 4·4%).

(viii) *Acetobenzylamide*, $C_6H_5 \cdot CH_2 \cdot NH \cdot CO \cdot CH_3$.—The nitration of this substance has been described by Amsel and Hofmann (*loc.*

cit.), who obtained aceto-*p*-nitrobenzylamide; but they do not mention any by-products. Having repeated the experiment, utilising our experience in the separation of the acetyl derivatives of *o*-, *p*-, and *m*-nitrobenzylamines, we have come to the conclusion that, although aceto-*o*- or -*m*-nitrobenzylamide (or both) is probably formed along with the *p*-compound, the quantity must be very small, for it could not be identified with certainty. This is in agreement with the rather strongly basic character of acetobenzylamide.

(ix) *Acetomethylbenzylamide*, $C_6H_5 \cdot CH_2 \cdot NMe \cdot CO \cdot CH_3$.—This substance was prepared by boiling methylbenzylamine with 2·5 parts of acetic anhydride for 15 minutes, and then boiling the product for a few minutes with excess of water. The oil, extracted with ether after the addition of excess of sodium hydroxide, gradually solidified on keeping in an evacuated desiccator and could then be crystallised from ether–ligroin (b. p. 40—60°), from which it separated in large, colourless cubes, m. p. 41—43°, b. p. 155°/16 mm. (Found: C, 73·3; H, 7·9. $C_{10}H_{13}ON$ requires C, 73·6; H, 8·0%). The same substance was obtained as a by-product in the preparation of dibenzylmethylamine described above. It is completely soluble in cold 3% hydrochloric acid.

The nitration was carried out by adding the substance in small portions to 10 parts of nitric acid (*d* 1·5) at − 10°. The liquid was allowed to warm during 1 hour to the ordinary temperature, and was then mixed with ice. No precipitation took place under this treatment, and the solution was therefore rendered alkaline and extracted with ether, when, on evaporation of the solvent, a solid residue was obtained which crystallised from ligroin in clusters of colourless needles, m. p. 80—81°. The substance also separated from alcohol–ligroin in stout prisms of the same m. p. It was identified as aceto-*p*-nitrobenzylmethylamide by analysis and by comparison with a synthetic specimen (below). The mother-liquors were carefully searched for an isomeride, but although a further quantity of the *p*-nitro-compound was obtained (total yield 90%), the *o*- and *m*-nitro-isomerides could not be identified with certainty, although traces of a more fusible compound were present.

Aceto-o-*nitrobenzylmethylamide*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NMe \cdot CO \cdot CH_3$, was prepared by Gabriel and Jansen's method.

Aceto-m-*nitrobenzylmethylamide* was prepared from the hydrochloride of *m*-nitrobenzylamine by boiling it (1 g.) for 15 minutes with acetic anhydride (4 c.c.) and anhydrous sodium acetate (1 g.). The product was warmed with water to decompose the excess of acetic anhydride, and the solution made alkaline and extracted with ether, from which, on evaporation, an oily residue was obtained

which quickly solidified, and, on crystallisation from benzene–ligroin, yielded colourless prisms, m. p. 56—57° (Found: C, 57·5; H, 5·9. $C_{10}H_{12}O_3N_2$ requires C, 57·7; H, 5·8%).

Aceto-p-*nitrobenzylmethylamide*, prepared similarly, separated from benzene–ligroin in colourless prisms, m. p. 80—81° (Found: C, 57·6; H, 6·0%).

(x) *Acetodibenzylamide*, $(C_6H_5\cdot CH_2)_2N\cdot CO\cdot CH_3$.—This substance was prepared by boiling dibenzylamine for a few minutes with acetic anhydride and decomposing the excess of the reagent with water. It was extracted from alkaline solution by means of ether, and, after distillation, was obtained as a rather viscous oil, b. p. 194—195°/3 mm. (Found: C, 79·9; H, 7·0. $C_{16}H_{17}ON$ requires C, 80·0; H, 7·1%). It was also prepared by treating a pyridine solution of dibenzylamine with acetyl chloride and extracting with ether after adding excess of dilute hydrochloric acid. It is easily soluble in concentrated hydrochloric acid, but only sparingly soluble in dilute acid. On boiling for 6 hours with 20% hydrochloric acid, hydrolysis of the acetyl group took place, and the solution on cooling deposited crystals of dibenzylamine hydrochloride.

Nitration with Different Concentrations of Nitric Acid.—(*a*) The acetyl compound (2·5 g.) was added in about 15 portions during 1½ hours to 15 g. of 95% nitric acid at about − 5°. At each addition a deep red colour was formed which vanished after a few seconds. The product was kept for a further hour at 0°, and at the ordinary temperature for the same period, and then mixed with ice. The oily precipitate slowly solidified and after crystallising from alcohol yielded 1·5 g. of crystals, m. p. 175°. After complete purification, these had m. p. 183° and were identified as aceto-*pp'*-dinitrodibenzylamide by direct comparison with a specimen of this substance, and by converting them by hydrolysis (boiling for 6 hours with 20% hydrochloric acid) into *pp'*-dinitrodibenzylamine which, along with its hydrochloride, was similarly identified. The alcoholic mother-liquors were evaporated and the residue was fractionally crystallised from alcohol, when aceto-*mm'*-dinitrodibenzylamide was readily isolated in a pure condition and identified by direct comparison with an authentic specimen (below). The ultimate residues yielded (besides a further quantity of the *pp'*-compound) a very small amount of the *oo'*-isomeride, which was obtained from gummy residues by seeding with a pure specimen. The quantities isolated were: *para* 45%; *meta* 20%; *ortho* 3%.

(*b*) The dibenzylamide was treated at 30—50° with 80% nitric acid, and the product isolated and separated as described above. Yields: *para* 30%; *meta* 40%; *ortho* trace.

(*c*) The dibenzylamide was boiled with 70% nitric acid for 15

minutes, and the products were isolated and separated. Yields: *para* 20%; *meta* 55%.

Aceto-oo'-*dinitrodibenzylamide*, $(NO_2 \cdot C_6H_4 \cdot CH_2)_2N \cdot CO \cdot CH_3$, was prepared from the corresponding base by acetylation with boiling acetic anhydride. After decomposing the acetic anhydride by boiling with water, sufficient additional acetic acid was added to complete the solution of the acetyl compound. On cooling, clusters of very pale yellow needles separated, m. p. 154° (Found: C, 58·6; H, 4·4. $C_{14}H_{15}O_5N_3$ requires C, 58·4; H, 4·5%).

Aceto-mm'-*dinitrodibenzylamide*, prepared in exactly the same way, crystallised in small, pale yellow prisms, m. p. 146° (Found: C, 58·5; H, 4·5%).

Aceto-pp'-*dinitrodibenzylamide*, obtained likewise, separated in colourless needles, m. p. 183—184° (Found: C, 58·3; H, 4·5%).

(xi) *Diacetylbenzylamine*, $C_6H_5 \cdot CH_2 \cdot N(CO \cdot CH_3)_2$.—Benzylamine (5 g.) was boiled with acetic anhydride (20 c.c.) for 3 days, after which the solution was cooled and shaken with water until the excess of acetic anhydride had decomposed. The solution was then made alkaline and extracted with ether. The residue from the ether evidently consisted of a mixture of mono- and di-acetyl derivatives, since some of the former compound crystallised on keeping for a few days in an evacuated desiccator. To isolate the diacetyl compound the mixture was dissolved in ether and the monoacetyl derivative removed by shaking with 5% hydrochloric acid. On evaporation of the ether an oil was obtained which refused to solidify and was therefore purified by distillation. Diacetylbenzylamine is a colourless, rather viscous liquid, b. p. 176—178°/30 mm. (Found: C, 69·1; H, 7·2. $C_{11}H_{13}O_2N$ requires C, 69·2; H, 6·9%). It is completely hydrolysed to benzylamine hydrochloride on boiling for 16 hours with 20% hydrochloric acid.

The substance was allowed to flow through a fine capillary tube into 10 parts of 95% nitric acid at — 20°, and the resulting solution mixed with crushed ice. The oily product thus obtained was extracted with ether after the addition of sodium hydroxide, and, as it did not solidify after evaporation of the ether, was hydrolysed by boiling for 12 hours with 20% hydrochloric acid. On evaporating the solution so obtained, a solid residue remained, consisting of *m*-nitrobenzylamine hydrochloride, which was readily isolated in the pure condition by crystallisation from alcohol, and identified by direct comparison with a genuine specimen. No by-product could be recognised.

Some of the analyses recorded in this paper were carried out by Mr. Arthur Rumfit, to whom the authors acknowledge their

indebtedness. They also desire to record their thanks to the Chemical Society for a grant wherewith part of the expense of this research has been defrayed.

THE UNIVERSITY, LEEDS. [*Received, May 2nd,* 1925.]

CCXLI.—*Syntheses of Disulphoxides.*

By DAVID TEMPLETON GIBSON, CECIL JAMES MILLER, and SAMUEL SMILES.

FOUR general methods of obtaining the disulphoxides are at present available, but the very simple synthesis from a mercaptan and a sulphonyl chloride, although frequently attempted, has not yet been successfully accomplished. Blomstrand (*Ber.*, 1870, **3**, 962)

(*a*) $RSO_2Cl + R'SH = HCl + RSO_2{\cdot}SR'$

claimed to have obtained tolyl amyl disulphoxide from amyl mercaptan and toluenesulphonyl chloride, but his product was ill-defined and apparently not analysed; thus Otto, after further investigation of the reaction, was fully justified in doubting this result (*Ber.*, 1882, **15**, 121). Otto also attempted to obtain diphenyl and ditolyl disulphoxides (*Ber.*, 1876, **9**, 1636; 1878, **11**, 2070) by this method, but was unsuccessful, isolating instead the corresponding disulphide and sulphinic acid. He represented the completed reaction as follows:

(*b*) $RSO_2Cl + 2RSH = HCl + RSO_2H + (RS)_2$.

Many other observers have since met with Otto's experience and agree with his representation of the process.

The circumstance that the disulphoxides apparently cannot be obtained in this manner has been utilised by Hinsberg (*Ber.*, 1903, **36**, 109) and by Fromm and Seixas Palma (*Ber.*, 1906, **39**, 3310) as evidence against the thiolsulphonate structure of these substances. Conclusive evidence in favour of this constitution has been obtained (J., 1924, **125**, 176; this vol., p. 224). Hence it seemed necessary to find an explanation of this discrepancy, and a further examination of the reaction between mercaptans and sulphonyl halides has now been made. In the reaction between disulphoxides and mercaptans the former undergo fission, yielding a sulphinic acid whilst the thioaryl group appears as disulphide (*loc. cit.*):

(*c*) $RSO_2SR' + R'SH = RSO_2H + (R'S)_2$.

Since this decomposition of the disulphoxides takes place very easily, it seemed probable that the reaction between sulphonyl halide and mercaptan may proceed in two stages, the disulphoxide

at first formed (according to *a*) being rapidly decomposed (compare *c*) by the mercaptan. According to this hypothesis it should be possible to obtain disulphoxides by the method if experimental conditions are adopted in favour of (*a*) and unfavourable to (*c*). In one set of experiments these have been attained by slowly adding the mercaptan to a large excess of the heated sulphonyl chloride, thus completing (*a*) as rapidly as possible and avoiding the excess of mercaptan necessary to (*c*). In other experiments the more reactive sulphonyl iodides were used, the secondary action of the mercaptan being to a great extent avoided by the use of silver mercaptides. With these modified conditions the method may be used for the synthesis of disulphoxides and, as shown below, the somewhat inaccessible class of disulphoxides containing dissimilar aromatic nuclei are readily obtained. Of the two methods described, that involving the use of the sulphonyl iodides is usually to be preferred, but owing to the tendency of these substances to liberate iodine some disulphide may be formed from the mercaptide. The success of this method is therefore more easily attained by using the more stable of the sulphonyl iodides and by choosing mercaptans which generate the soluble disulphides. The latter condition facilitates separation of the impurity from the required disulphoxide.

It is now evident that the failure to obtain disulphoxides from these reagents under ordinary conditions can no longer be used as objection to the thiolsulphonate structure; on the contrary, the results now described give further evidence in support of this.

Experimental.

(a) *Syntheses from Mercaptans and Sulphonyl Chlorides.*—The conditions adopted were as follows. A solution of the mercaptan in benzene containing a small quantity of pyridine was slowly added to a boiling solution of excess of the sulphonyl chloride in the same solvent. When the liquid had cooled, any sulphinic acid, pyridine, and the excess of acid chloride present were removed. The solvent was evaporated and the residue was examined.

Di-*p*-tolyl disulphoxide was obtained in 25% yield from 2 mols. of the mercaptan and 5 mols. of *p*-toluenesulphonyl chloride. It was isolated and identified in the usual manner.

2 : 5 : 2′ : 5′-Tetrachlorodiphenyl disulphoxide was obtained (5% yield) from 2 : 5-dichlorothiophenol (1 mol.) and 2 : 5-dichlorobenzenesulphonyl chloride (7 mols.). The product (m. p. 127°) was identified in the usual manner.

4-*Tolyl* 3-*nitrobenzenethiolsulphonate*, $C_6H_4Me{\cdot}S{\cdot}SO_2{\cdot}C_6H_4{\cdot}NO_2$, was isolated (30% yield) from the reaction between 3-nitrobenzene-

sulphonyl chloride (8 mols.) and 4-tolyl mercaptan (1 mol.). The substance, isolated as usual, formed colourless needles, m. p. 109° (Found: C, 50·4; H, 3·6; N, 4·9. $C_{13}H_{11}O_4NS_2$ requires C, 50·5; H, 3·5; N, 4·5%).

The ascribed constitution was confirmed by treating the substance in warm alcohol with 2 : 5-dichlorothiophenol (1 mol.). 3-Nitrobenzenesulphinic acid and 2 : 5-dichloro-4′-methyldiphenyl disulphide were isolated (J., 1924, **125**, 182).

(b) *Syntheses from Sulphonyl Iodides and Silver Mercaptides.*—The sulphonyl iodides (Otto and Tröger, *Ber.*, 1891, **24**, 478) were prepared by slowly adding an alcoholic solution of the theoretical amount of iodine to a cold solution of the sodium sulphinate containing about 20 g. of the salt in 2—3 litres of water. The crystalline material was washed and dried (yield, under the best conditions, generally over 80%).

2 : 5-*Dichlorobenzenesulphonyl iodide*, $C_6H_3Cl_2{\cdot}SO_2I$, separated from light petroleum in golden-yellow needles, m. p. 100° (Found: Cl + I, 58·7; S, 9·35. $C_6H_3O_2Cl_2IS$ requires Cl + I, 58·7; S, 9·6%).

Naphthalene-2-sulphonyl iodide, $C_{10}H_7{\cdot}SO_2I$, separated from benzene–light petroleum in yellow needles, m. p. 96—97° (decomp.). This sulphonyl iodide was more stable in solution than any other encountered in these experiments (Found: I, 40·0; S, 10·0. $C_{10}H_7O_2IS$ requires I, 39·9; S, 10·0%).

The silver mercaptides used were obtained from silver nitrate, the mercaptan, and sodium acetate (1 mol.) in alcoholic solution.

The dry silver mercaptide (rather more than 1 mol.) was gradually added with thorough shaking to a dry solution of the sulphonyl iodide in ether or benzene. Owing to the tendency of solutions of the iodides spontaneously to liberate iodine, the duration of the process was kept within certain limits—generally about ½ hour—which varied with different sulphonyl iodides. The silver halide was then removed and the solution was treated with a little dilute aqueous sodium carbonate and, if necessary, with sufficient sodium sulphite to remove free iodine. After the solvent had been removed the residue was purified in the usual manner. In this way the following thiolsulphonates were obtained.

2 : 5-Dibromophenyl 2 : 5-dichlorobenzenethiolsulphonate,

$$C_6H_3Br_2{\cdot}S{\cdot}SO_2{\cdot}C_6H_3Cl_2,$$

from 2 : 5-dichlorobenzenesulphonyl iodide and 2 : 5-dibromophenyl mercaptan (88% yield). The product (m. p. 124°) was identified with that obtained from silver dichlorobenzenesulphinate and dibromophenylsulphur bromide (this vol., p. 230) (Found: S, 13·3. Calc., S, 13·4%).

4-Tolyl 2 : 5-*dichlorobenzenethiolsulphonate*, $C_6H_4Me{\cdot}S{\cdot}SO_2{\cdot}C_6H_3Cl_2$, was obtained (80% yield) from 2 : 5-dichlorobenzenesulphonyl iodide and silver 4-tolyl mercaptide. The subtance separated from aqueous alcohol in small, colourless needles, m. p. 74° (Found: S, 19·2; Cl, 21·4. $C_{13}H_{10}O_2Cl_2S_2$ requires S, 19·25; Cl, 21·2%).

6-Methoxy-3-tolyl 2-naphthalenethiolsulphonate, $OMe{\cdot}C_6H_3Me{\cdot}S{\cdot}SO_2{\cdot}C_{10}H_7$, was prepared (about 85% yield) from 2-naphthalenesulphonyl iodide and 4-methoxytoluene 3-mercaptan (J., 1923, **123**, 2390). After purification from hot alcohol the substance formed colourless prisms, m. p. 113—114° (Found: C, 62·6; H, 4·7; S, 18·5. $C_{18}H_{16}O_3S_2$ requires C, 62·7; H, 4·6; S, 18·6%).

2 : 4-*Xylyl 2-naphthalenethiolsulphonate*, $C_6H_3Me_2{\cdot}S{\cdot}SO_2{\cdot}C_{10}H_7$, was obtained (about 85% yield) from 2-naphthalenesulphonyl iodide and 2 : 4-xylylthiol. It separated from benzene–ligroin in colourless prisms, m. p. 80—81° (Found: C, 65·5; H, 4·9; S, 19·2. $C_{18}H_{16}O_2S_2$ requires C, 65·8; H, 4·9; S, 19·5%).

We are indebted to the Chemical Society for a grant which partly defrayed the cost of these experiments.

THE UNIVERSITY, GLASGOW.
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CCXLII.—*Studies of Electrolytic Polarisation. Part III. The Diffusion Layer.*

By SAMUEL GLASSTONE.

SINCE Noyes and Whitney (*Z. physikal. Chem.*, 1897, **23**, 689) first put forward the view that diffusion plays the chief part in the rate of a heterogeneous process such as solution, and Nernst *et al.* (*ibid.*, 1904, **47**, 52; 1905, **53**, 235) extended the idea to chemical and electrochemical reactions in heterogeneous systems, most authors have accepted the idea of the existence of a layer of liquid of different concentration from that of the bulk of the solution at the surface of the reacting solid or the electrode in the case of an electrolytic process. The thickness of this layer has been presumed to be independent of the concentration of the liquid, and even to vary only slightly with the nature of the two phases involved in the reaction. Further, in the case of electrolytic reduction Jahn ("Grundriss der Elektrochemie," 1905, p. 519 *et seq.*) quotes results from the work of Haber *et al.* (*Z. physikal. Chem.*, 1900, **32**, 193, 271; 1904, **47**, 257) and from that of Akerberg (*Z. anorg. Chem.*,

1902, **31**, 161) which indicate that the thickness of the diffusion layer for a given electrode and electrolyte is also independent of the current density under such conditions that very little or no gas is being evolved. The results obtained by Nernst and Merriam (*Z. physikal. Chem.*, 1905, **53**, 235) and by Wilson and Youtz (*J. Ind. Eng. Chem.*, 1923, **15**, 603), as well as unpublished measurements by the present author, all lead to the same conclusion. When a heterogeneous reaction involves the liberation of gas, as in the dissolution of metals in acid, the results of Palmaer (*Z. physikal. Chem.*, 1906, **56**, 689) and of Prins (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **23**, 1449) indicate that it is very probable that the thickness of the diffusion layer does not remain constant; no work, however, appears to have been done in connexion with the diffusion layer in an electrolytic process involving free evolution of gas, but the results described below have an important bearing on this problem. These results were obtained in the course of experiments on lead and mercury cathodes in various electrolytes, some of the results of which have already been published (J., 1924, **125**, 2414, 2646). An examination of the figures given in these papers will show that under a variety of conditions the difference between the direct and the extrapolated overvoltage, which is presumably due to the resistance at the electrode surface, is not nearly proportional to the magnitude of the current. This indicates that the value of the resistance alters with the current as long as gas bubbles are being evolved; actually the resistance decreases as the current is increased. A large part of this resistance is believed to be due to the presence of a thin layer of dilute electrolyte—the diffusion layer—which is in immediate contact with the electrode; it thus appears that the resistance, and probably the thickness, of this layer decreases as the current density is increased. This is no doubt due to the fact that the rapid evolution of gas at the high current densities causes a stirring of the electrolyte which results in a reduction of the thickness of the diffusion layer. Further confirmation of this view has been obtained by experiments with a mercury cathode in dilute solutions of sulphuric acid containing potassium sulphate, and with various electrodes in hydrochloric acid solution.

The experimental results have thrown further light on the factors influencing the rate of fall of the back *E.M.F.* of a polarised electrode; in the previous work on the mercury cathode (*loc. cit.*) it was shown that the diffusion of oxygen from the anode can affect the back *E.M.F.* and it is now found that the thickness of the diffusion layer may also influence the rate of fall.

EXPERIMENTAL.

The apparatus used in this work was the same as that described in previous communications (*loc. cit.*); unless otherwise stated, the experiments were carried out at room temperature (about 15°) and anode and cathode compartments were not separated.

Sulphuric Acid and Potassium Sulphate Solutions.—During the course of the measurements of the overvoltage at the mercury cathode in $N/16$-sulphuric acid containing potassium sulphate (see J., 1924, **125**, 2651) it was found that, although the back *E.M.F.* of the electrode decreased normally for the first 0·012 sec. after the polarising current was switched off, yet in certain cases, after this period had elapsed, an abnormal condition set in which was independent of the nature of the electrode vessel, and of the separation or not of the anode and cathode compartments. The following typical result will make this abnormality clear:

Back *E.M.F.* after:	C.D. (amp./cm.^{2})	0·003	0·006	0·012	0·024
0·012 sec.		0·91	0·92	0·92	0·92
0·018 „		0·89	0·89	0·85	0·85

After a certain interval of time, instead of the normal decrease of the back *E.M.F.* there was a sudden, more rapid, fall of potential. This fall was first observed at the highest current densities used, but after increasing time intervals it was found to occur at lower current densities. At a higher temperature the sudden fall of potential took place after a shorter interval of time for any particular current density. This curious behaviour was noted in all cases where the electrolyte contained an excess of potassium ions and where the potentials indicated that the normal hydrogen discharge was not the only cathodic process. Similar experiments in which sodium sulphate was used instead of the potassium salt gave similar results.

The potential measurements suggest that the hydrogen-ion concentration in the vicinity of the electrode in these solutions is impoverished, probably owing to the fact that the presence of a large excess of potassium ions prevents the hydrogen ions from diffusing up to the electrode as fast as they are discharged; the potential of the electrode becomes more negative and potassium ions are discharged to form an amalgam. When the polarising current is switched off, the hydrogen ions can diffuse through the impoverished layer of electrolyte without being discharged and so react with the amalgam, causing its rapid decomposition (see Klein, *Z. anorg. Chem.*, 1924, **137**, 39) and a consequent fall of potential; the thinner the diffusion layer the sooner will this sudden fall of potential occur. The results given above show that this fall occurs

soonest at the highest current densities, and hence we may conclude that under conditions of gas evolution the diffusion layer is thinnest at high current densities. An increase of temperature causes the rate of diffusion to increase, even if it does not appreciably influence the thickness of the diffusion layer, and so the time interval between switching off the current and the sudden fall of back *E.M.F.* is diminished. These conclusions regarding the diffusion layer in the special case under discussion are in agreement with those arrived at from a consideration of the difference between the direct and the extrapolated overvoltage measurements.

If the above views are correct it is to be expected that rapid stirring of the electrode and electrolyte will have some influence on the fall of the back *E.M.F.* In these circumstances the diffusion layer would cease to exist the instant that the polarising current was switched off, and so a more rapid fall of potential right from the beginning would be expected at all current densities, but no sudden fall after an interval of time. These forecasts have been confirmed; up to 0·03 sec. after the polarising circuit was broken the rate of fall of the back *E.M.F.* was still normal at all the current densities used in the previous experiments; this rate of fall was greater initially than in a similar experiment in which the electrolyte was not stirred. The following figures illustrate the effect of stirring.

Back *E.M.F.* after:	C.D. amp./cm.^{2}	0·002	0·004	0·008	0·016	
0·002 sec.		0·98	1·00	1·02	1·04	Not stirred.
0·006 ,,		0·95	0·97	0·99	1·01	
0·018 ,,		0·88	0·90	0·91	0·89	
0·002 ,,		0·92	0·94	0·96	0·99	Stirred.
0·006 ,,		0·87	0·89	0·91	0·94	
0·018 ,,		0·81	0·83	0·85	0·87	

Hydrochloric Acid Solutions.—In the course of experiments with *N*-hydrochloric acid as electrolyte, chlorine gas was always evolved at the anode. If the anode and cathode compartments were separated, no special precautions were taken before making measurements; in other cases the polarising current was passed for some time so that the electrolyte dissolved a considerable amount of chlorine gas. In the latter circumstances no hydrogen could be liberated at the cathode unless a high current density was applied, *e.g.*, 0·24 amp. per 10 sq. cm., but once gas evolution had commenced the current could be reduced by gradual stages to 0·015 amp. and the evolution of gas would continue. If the current was reduced suddenly, gas evolution ceased. In making measurements it was usual to determine the potential by the direct method first, and then to measure the back *E.M.F.* at certain definite times after the

polarising current was switched off, first with decreasing and then with increasing current densities. The results quoted below are the mean of those obtained with increasing and decreasing currents; the actual values for the same current density did not vary appreciably.

The following table contains the results obtained with a mercury cathode of 10 sq. cm. exposed area in *N*-hydrochloric acid; the anode and cathode compartments were not separated.

C.D.	Overvoltage.		Back *E.M.F.* after :					
(amp./cm.²).	Direct.	Extrap.	0·002	0·004	0·006	0·008	0·012	0·018 sec.
0·0015	1·03	1·01	0·98	0·96	0·94	0·91	0·89	0·84
0·003	1·07	1·03	1·00	0·98	0·96	0·91	0·89	0·84
0·006	1·11	—	0·99	0·97	0·95	0·89	0·84	*0·74
0·012	1·15	—	0·97	0·94	0·89	0·80	*0·67	0·50
0·024	1·19	—	0·93	0·89	0·83	*0·67	0·49	0·28

These results show that there are two distinct abnormalities in the fall of the back *E.M.F.* after the polarising current is switched off. In the first place, although the direct overvoltage increases regularly, yet the back *E.M.F.* after 0·002 sec. at first increases and then decreases as the current density is increased. This suggests that immediately the current is switched off at the high current densities there is a very rapid fall of potential which cannot be detected directly. Following this the rate of fall of potential is fairly regular until after a certain interval of time there is another sudden fall in the back *E.M.F.* at the points marked with an asterisk in the above table. The period of time that elapses before this second fall of potential occurs decreases as the current density is increased. This fall of potential is not due to the failure of the electrode to reach its equilibrium condition when the current is switched on, since measurements have shown that at these high current densities almost the same potential is reached while the current is flowing whether the commutator is working or not.

In the next experiments the anode and cathode compartments were separated by placing the mercury in a porous pot; the platinum anode was placed in the liquid which surrounded the pot. The same electrolyte, *N*-hydrochloric acid, was used throughout. The results were as follows.

C.D.	Overvoltage.		Back *E.M.F.* after			
(amp./cm.²).	Direct.	Extrap.	0·002	0·004	0·006	0·012 sec.
0·0015	1·03	1·01	0·98	0·96	0·94	0·89
0·003	1·07	1·03	0·99	0·97	0·95	0·89
0·006	1·11	1·04	1·00	0·98	0·96	0·90
0·012	1·15	1·05	1·01	0·99	0·97	0·91
0·024	1·19	1·06	1·02	0·99	0·97	0·91

These figures appear to be quite normal in every way, and hence it may be concluded that the abnormal fall of the back *E.M.F.*

observed in the previous experiment is due to the action of the chlorine gas liberated at the anode; in all cases where the chlorine was prevented from diffusing to the cathode the fall of potential was normal, but in other cases it was abnormal. In order to determine the influence, if any, of the material of the electrode vessel on the abnormal results, the platinum anode was placed inside the porous pot containing the mercury; the potentials were almost the same as those obtained with the mercury in a glass beaker, and hence the experiment did not yield any decisive result. Using a glass beaker which had been standing with concentrated alkali for about a week, the following back *E.M.F.'s* were measured at 0·002 sec. after the polarising current was switched off :—

C.D.	0·0015	0·003	0·006	0·012	0·024
Back *E.M.F.*	0·96	0·97	0·95	0·91	0·80

The inside of the beaker was then coated with paraffin wax and the following measurements were then recorded at the same series of current densities :—

Back *E.M.F.*	0·96	0·97	0·98	0·97	0·95

The initial fall in the back *E.M.F.* at high current densities is thus influenced to some extent by the material of the electrode vessel, and different results were obtained from time to time with different glass beakers. The sudden fall that occurred after the lapse of an interval of time was always observed, provided the anode and cathode compartments were not separated.

Discussion.

Applying the suggestions that have been put forward to explain the abnormal back *E.M.F.* of the mercury cathode in dilute sulphuric acid solutions (see Part II, *loc. cit.*), it appears that the first rapid fall of potential at the high current densities is to be attributed to the concentration of the electromotively active material at the circumference of the electrode owing to the action of surface tension forces. As soon as the polarising current is switched off this active substance appears to be rapidly attacked by the chlorine in solution, and the material of the electrode vessel may influence the rate of reaction; there is thus a rapid initial fall of potential. If the mercury was in such a condition that the surface forces were no longer operative, then this rapid fall of potential should not be observed; some experiments were therefore made with an amalgamated lead electrode, which in most cases gives overvoltages that are not very different from those given by pure mercury. The electrodes used had an exposed area of 7·5 sq. cm. and the direct overvoltages were almost the same as those observed with a

pure mercury surface of the same area. The back *E.M.F.*'s measured at 0·002 sec. after the polarising current was switched off increased regularly as the current density increased independent of whether the anode and cathode compartments were separated or not, and showed no signs of abnormality.

C.D. (amp./cm.^{2})	0·004	0·008	0·016	0·032
Direct overvoltage	1·07	1·11	1·15	1·18
Back *E.M.F.* after 0·002 sec.	0·87	0·88	0·90	0·93

The subsequent rate of fall of the back *E.M.F.* was too great to make extrapolation possible, and so the actual overvoltages can only be inferred from the direct measurements. The decrease of back *E.M.F.*, although rapid, was quite regular in those cases in which the anode and cathode compartments were separated, but when this was not the case a sudden fall of potential was observed after an interval of time had elapsed; first at the higher current densities, and after increasing periods at the lower current densities. It appears therefore that the initial sudden fall of potential observed with the mercury cathode in the presence of dissolved chlorine is connected with the surface tension forces that are operative when the current is flowing, but the subsequent rapid fall after an interval of time is due to another cause.

According to the views expressed in connexion with the abnormal results obtained with the mercury cathode in sulphuric acid containing potassium sulphate, the sudden fall of potential that is observed some time after the polarising current is switched off is apparently due to the diffusion of chlorine through the layer of electrolyte in immediate contact with the electrode. Judging by the difference between the direct and the extrapolated overvoltages, this layer should be thinnest at the highest current densities, and consequently under these conditions chlorine will take the least time to diffuse through. By removing the active hydrogen very rapidly, the chlorine causes a sudden fall of potential, which will occur soonest at the high current densities; the two tables given above show that the time which elapses between switching off the current and the commencement of this rapid fall of potential is roughly proportional to the resistance which is the cause of the difference between the direct and the extrapolated overvoltages. Since this rapid fall of potential could not be connected in any way with the material of the electrode or of the cell, but should depend simply on the existence of a diffusion layer, it should occur with other electrodes in hydrochloric acid. Experiments with lead and copper electrodes have shown that this is actually the case; although neither of them showed the very rapid initial fall of the back *E.M.F.* that occurred with the mercury cathode, yet in both

cases there was a sudden fall of potential after a certain interval of time; this interval was shortest at the highest current densities. Where the anode and cathode compartments were separated before the electrolyte had dissolved any chlorine gas this rapid fall of potential was not observed in any case investigated hitherto.

Since both types of abnormal back *E.M.F.* are connected in some way with the chlorine gas dissolved in the electrolyte, but in one case the fall takes place almost the instant the current is switched off, whilst in the other only after an appreciable interval of time, it is clear that in the former case the diffusion layer must be extremely thin. This means that the layer of solution containing dissolved chlorine must be almost in direct contact with the mercury at its circumference, since it is considered that it is there that the first rapid removal of active material occurs immediately the current is switched off. It is possible that the forces acting at the electrode–electrolyte interface under the influence of the current cause fresh electrolyte containing dissolved chlorine to be drawn continuously towards the circumference of the electrode, and so no appreciable time elapses for the chlorine to diffuse in. When the current is off, the surface forces are no longer operative, and so fresh electrolyte is no longer drawn to the circumference of the mercury, neither is there such a large concentration of active material in this vicinity; hence the subsequent fall of potential is not very rapid until chlorine diffuses up to the main portion of the electrode surface.

Summary.

An examination of the difference between the direct and the extrapolated overvoltages at lead and mercury cathodes in various electrolytes has led to the conclusion that the thickness of the diffusion layer at an electrode from which gas is being liberated freely decreases as the current density is increased; this is probably due to the stirring caused by the rapid evolution of bubbles. This view has been confirmed by an analysis of the abnormal fall in the back *E.M.F.* of a mercury cathode in a dilute solution of sulphuric acid containing an excess of alkali sulphate, and of various cathodes in *N*-hydrochloric acid saturated with chlorine. In previous work it has been found that oxygen diffusing from the anode may influence the initial fall of the back *E.M.F.* of a mercury cathode in a manner which depends on the material of the electrode vessel and the current density; a similar abnormality has been observed as the result of the diffusion of anodic chlorine towards a mercury cathode in hydrochloric acid solution.

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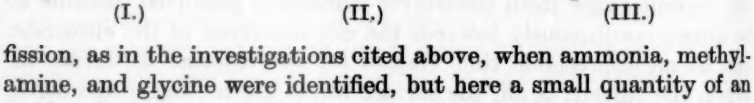
CCXLIII.—*The* 4- *and* 5-*Nitro*-1 : 2-*Dimethylglyoxalines.*

By VINAYAK KESHAV BHAGWAT and FRANK LEE PYMAN.

IN the methylation of 4(5)-nitroglyoxaline (Hazeldine, Pyman, and Winchester, J., 1924, **125**, 1431) and 4(5)-nitro-5(4)-methylglyoxaline (Pyman, J., 1922, **121**, 2616) by methyl sulphate, 350 and 233 times respectively as much of the isomerides with NO_2 : (*N*)Me in the 5 : 1-positions were isolated as of those with NO_2 : (*N*)Me in the 4 : 1-positions. Under similar conditions, 4(5)-nitro-2-methylglyoxaline (I) yields 5-*nitro*-1 : 2-*dimethylglyoxaline* (II) and 4-*nitro*-1 : 2-*dimethylglyoxaline* (III) in the relative proportion 50 : 1. The constitution of the first of these (and therefore of the other also) was determined by reduction and



(I.) (II.) (III.)

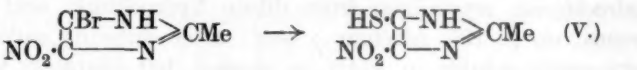
fission, as in the investigations cited above, when ammonia, methylamine, and glycine were identified, but here a small quantity of an unidentified base, $C_5H_{10}N_2$, was also obtained. On nitrating 1 : 2-dimethylglyoxaline, the 4- and 5-nitro-derivatives were isolated in the relative proportion 2 : 1, this result being similar to that obtained by the nitration of 1-methylglyoxaline (Hazeldine, Pyman, and Winchester, *loc. cit.*). The 5-nitro-compound gave a picrate and is thus a stronger base than the 4-isomeride, from which no picrate could be prepared. Moreover, the 5-isomeride combines with methyl iodide at 100°, whereas the 4-isomeride does not react with methyl iodide at 100°, although it does so at 150°. The methiodides of the two isomerides are identical, being 4(5)-nitro-1 : 2 : 3-trimethylglyoxalinium iodide, which yields on distillation 4-nitro-1 : 2-dimethylglyoxaline. The properties of the isomerides are thus generally similar to those of the 5- and 4-nitro-1-methylglyoxalines.*

The reactivity of the 2-methyl group in these compounds has been examined. Since the bromine atom in 2-bromo-5-nitro-1 : 4-dimethylglyoxaline can be replaced by the sulphonic acid residue (Pyman and Timmis, J., 1923, **123**, 494), it was thought that 5-nitro-1 : 2-dimethylglyoxaline might react with benzaldehyde to yield 5-nitro-2-styryl-1-methylglyoxaline under the conditions used by Windaus and Langenbeck (*Ber.*, 1923, **56**, 683) for converting 4(5)-nitro-5(4)-methylglyoxaline into 4(5)-nitro-5(4)-styrylgly-

* It is shown in the experimental part that the behaviour of the pair of isomerides 4(and 5)-nitro-1 : 5(and 1 : 4)-dimethylglyoxalines is similar.

oxaline, but neither 4- nor 5-nitro-1 : 2-dimethylglyoxaline reacted with benzaldehyde, and the result calls to mind an unsuccessful attempt to condense 2-methylglyoxaline-4(5)-sulphonic acid with benzaldehyde (Forsyth, Moore, and Pyman, J., 1924, **125**, 919).

5(4)-Bromo-4(5)-nitro-2-methylglyoxaline (IV) is very easily converted into the ammonium salt of 4(5)-*nitro*-5(4)-*thiol*-2-*methylglyoxaline* (V) by means of ammonium sulphide.



EXPERIMENTAL.

The 4- and 5-Nitro-1 : 2-dimethylglyoxalines.

(A) *Preparation by Nitration of 1 : 2-Dimethylglyoxaline.*—Concentrated sulphuric acid (6 c.c.) was added to 1 : 2-dimethylglyoxaline (3 g.) in nitric acid (6 c.c.; *d* 1·4) at 0°, the product heated for 4 hours at 100°, cooled, and aqueous sodium hydroxide added, when nearly pure 4-nitro-1 : 2-dimethylglyoxaline (0·5 g.) separated. Chloroform extracted from the filtrate a mixture of bases which was separated by ether into sparingly soluble and readily soluble fractions (0·9 and 2·0 g.), the latter consisting largely of 1 : 2-dimethylglyoxaline. After fractional crystallisation as picrate or base, there were isolated in almost pure condition 4-nitro-1 : 2-dimethylglyoxaline (yield 20% *), 5-nitro-1 : 2-dimethylglyoxaline (yield 10%), and unchanged 1 : 2-dimethylglyoxaline (yield 22%).

(B) *Preparation by Methylation of 4(5)-Nitro-2-methylglyoxaline.*—4(5)-Nitro-2-methylglyoxaline (20 g.) and methyl sulphate (16 c.c.) were heated for 1 hour at 100°, and the products worked up as in analogous cases described previously (*e.g.*, J., 1922, **121**, 2616), when 2·0 g. of 4(5)-nitro-2-methylglyoxaline were recovered, whilst 5-nitro-1 : 2-dimethylglyoxaline was isolated as picrate (33 g., pure, yield 57%), and 4-nitro-1 : 2-dimethylglyoxaline as base (0·25 g., pure, yield 1·1%).

4-*Nitro*-1 : 2-*dimethylglyoxaline* (III) crystallises from alcohol in glistening needles, m. p. 182—183° (corr.). It is easily soluble in alcohol, somewhat sparingly soluble in cold water, and sparingly soluble in ether (Found: C, 42·4; H, 5·0. $C_5H_7O_2N_3$ requires C, 42·6; H, 5·0%).

The *hydrochloride* is obtained on spontaneous evaporation of a solution of the base in concentrated hydrochloric acid in long needles which on rapid heating sinter at about 175° and melt with

* The compounds described in this paper were colourless, and yields are given in percentage of the theoretical, except where it is stated to the contrary.

effervescence at about 215°. It dissociates on heating at 100° or on treatment with water, giving the base. The base did not yield a picrate.

5-*Nitro*-1 : 2-*dimethylglyoxaline* (II) crystallises from water in long, stout needles, m. p. 138—139° (corr.). It is easily soluble in alcohol, and somewhat sparingly soluble in cold water or ether (Found : C, 42·4; H, 5·1. $C_5H_7O_2N_3$ requires C, 42·6; H, 5·0%). The *hydrochloride* crystallises from dilute hydrochloric acid in large prisms, m. p. 195° (decomp.; corr.) after sintering earlier. It is very easily soluble in water or alcohol, but sparingly soluble in acetone. It is not dissociated by water, and remains unchanged in m. p. after prolonged heating at 100°, but the salt is slowly volatilised. The *picrate* crystallises from water or alcohol in yellow needles, m. p. 162—163° (corr.). It is very sparingly soluble in these solvents when cold (Found : C, 35·8; H, 3·0. $C_5H_7O_2N_3,C_6H_3O_7N_3$ requires C, 35·7; H, 2·7%).

4(5)-*Nitro*-1 : 2 : 3-*trimethylglyoxalinium iodide* is formed on heating methyl iodide with 5-nitro-1 : 2-dimethylglyoxaline at 100° (but not on heating under reflux), or with 4-nitro-1 : 2-dimethylglyoxaline at 150° but not at 100°. It crystallises from alcohol in bright yellow needles, m. p. 195—196° (decomp.; corr.). It is soluble in water and rather less so in cold acetone (Found : I, 44·8. $C_6H_{10}O_2N_3I$ requires I, 44·9%). On heating this salt (3 g.) over a free flame under 33 mm. until distillation began, and crystallising the combined distillate and residue from alcohol, 4-nitro-1 : 2-dimethylglyoxaline (1·0 g., m. p. 179—180°, yield 67%) was obtained.

Attempted Condensations with Benzaldehyde.—Both 4- and 5-nitro-1 : 2-dimethylglyoxalines were recovered to the extent of 90% unchanged after heating 1 g. with benzaldehyde (2 c.c.) and piperidine (0·2 c.c.) for 2 hours at 155—160° under reflux.

Reduction of 5-*Nitro*-1 : 2-*dimethylglyoxaline.*—To a solution of the base (14 g.) in concentrated hydrochloric acid (50 c.c.), a solution of hydrated stannous chloride (68 g.) in concentrated hydrochloric acid (150 c.c.) was added below 10°. After keeping over-night, tin was removed by hydrogen sulphide, when partly crystalline hydrochlorides were obtained. On extraction with absolute alcohol, ammonium chloride (6 g.) remained undissolved; the extract was then added to a solution of picric acid (25 g.) in hot water (1 l.), when picrates were deposited from which after repeated crystallisation from water and alcohol, 1·5 g. of a *picrate*, m. p. 142·5° (corr.), were obtained (Found : C, 39·7, 39·4, 39·1, 39·1; H, 3·7, 4·0, 3·9, 3·8. N, 21·7, 21·7, 21·4. $C_5H_{10}N_2,C_6H_3O_7N_3$ requires C, 40·4; H, 4·0; N, 21·4%). The mother-liquor was extracted with ether to remove

picric acid, and evaporated to dryness, when about 7 g. of partly crystalline hydrochlorides were obtained. These were separated by the method used by Hazeldine, Pyman, and Winchester (*loc. cit.*, p. 1435) into ammonium chloride (1·0 g.), crude methylamine hydrochloride (1·6 g. containing 54·0% Cl) and the hydrochloride of glycine ethyl ester (0·8 g., m. p. 136—140°), yielding the pure substance, m. p. 143—144° (corr.; alone or mixed with a synthetic specimen).

4(5)-*Nitro*-5(4)-*thiol*-2-*methylglyoxaline* (V).—Hydrogen sulphide was passed through a warm solution of 5(4)-bromo-4(5)-nitro-2-methylglyoxaline (2 g.) in 5*N*-ammonia (15 c.c.) for ¼ hour, when the *ammonium* salt of 4(5)-nitro-5(4)-thiol-2-methylglyoxaline separated in deep yellow prisms * (1·7 g., yield almost theoretical). It is readily recrystallised from water, and both the crude and the purified material darken from 190°, being quite black by 210° (corr.). This salt is anhydrous, and yields ammonia when boiled with aqueous sodium hydroxide (Found: C, 27·6; H, 5·0; N, 31·9; S, 18·3. $C_4H_8O_2N_4S$ requires C, 27·3; H, 4·5; N, 31·8; S, 18·2%). On rendering its aqueous solution faintly acid with hydrochloric acid, 4(5)-*nitro*-5(4)-*thiol*-2-*methylglyoxaline* is obtained as a yellow, crystalline precipitate, m. p. *ca.* 260° (corr.; decomp.) crude or after crystallisation from alcohol (Found: C, 30·3, 29·8; H, 3·5, 3·2. $C_4H_5O_2N_3S$ requires C, 30·2; H, 3·1%). It is sparingly soluble in alcohol or hot water, and readily soluble in alkalis, ammonia, and sodium carbonate, giving bright yellow solutions, whilst sodium hydroxide gives an orange-yellow solution, which reddens on keeping. It dissolves in 5*N*-hydrochloric acid, but the solution soon deposits pale buff crystals of the hydrochloride, m. p. *ca.* 260° (corr.; decomp.), which dissociate on treatment with water.

4(5)-*Nitro*-1 : 3 : 5(4)-*trimethylglyoxalinium iodide* is formed on heating methyl iodide with 5-nitro-1 : 4-dimethylglyoxaline under reflux or with 4-nitro-1 : 5-dimethylglyoxaline at 100° (but not under reflux). It crystallises from acetone in bright yellow, prismatic needles, m. p. (of material dried at 100°) 134—135° (corr.), and is readily soluble in water or alcohol, but sparingly soluble in cold acetone (Found: loss in a vacuum, 2·9. $C_6H_{10}O_2N_3I,\frac{1}{2}H_2O$ requires H_2O, 3·1. Found, in dried salt: I, 44·9. $C_6H_{10}O_2N_3I$ requires I, 44·9%). After heating the air-dried salt (6 g.) under diminished pressure until all methyl iodide was removed, and crystallising the residue from water, 4-nitro-1 : 5-dimethylglyoxaline (2·42 g., pure, yield 83%) was obtained, whilst the mother-liquors, after being mixed with picric acid and seeded with 5-nitro-1 : 4-dimethylglyoxaline picrate, deposited a minute quantity of a crystal-

* The formation of crystals in this way was first observed by Mr. L. Light, M.Sc.Tech.

line picrate. 4-Nitro-1 : 5-dimethylglyoxaline dissolves in concentrated hydrochloric acid, but after spontaneous evaporation in the air the base remains. On adding water to the solution of the base in concentrated hydrochloric acid, the base is precipitated.

5-Nitro-1 : 4-dimethylglyoxaline hydrochloride crystallises from dilute hydrochloric acid in prisms, which, after drying at 100°, melt and decompose at 188° (corr.). It slowly volatilises at 100°. After evaporation with water it can be recovered unchanged.

One of us (V. K. B.) desires to thank the University of Bombay for a Sir Mangaldas Nathubai Technical Scholarship which has enabled him to take part in the investigation.

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CCXLIV.—*Some Physical Properties of Aniline and its Aqueous Solutions.*

By MALCOLM PERCIVAL APPLEBEY and PERCIVAL GLYN DAVIES.

IN the course of work on the osmotic properties of aniline solutions (see following paper) the authors have had occasion to prepare this liquid in a pure condition and to make some measurements of its principal properties, as well as to investigate the effect of water upon those properties.

The aniline, purified from thiophen compounds by the method of Hantzsch and Freese (*Ber.*, 1894, **27**, 3), was finally dried over solid potash and fractionated in an apparatus shielded from atmospheric moisture and carbon dioxide by soda-lime tubes. It showed no brown colour, but had a bright blue fluorescence and boiled well within half a degree. The fluorescence disappeared in the course of a few days, even when the liquid was kept in closed brown stoppered bottles in a desiccator in a dark cupboard.

The physical properties of purified aniline have been measured by Timmermans (*Proc. Roy. Soc. Dublin*, 1912, **13**, 326), Knowles (*J. Ind. Eng. Chem.*, 1920, **12**, 881), Schwers (*J. Chim. Phys.*, 1911, **9**, 15), and Tyrer (J., 1911, **99**, 872; 1912, **101**, 84). Their values are compared with ours in the following table :—

	Applebey and Davies.	Timmermans.	Knowles.	Schwers.	Tyrer.
F. p.	−5·98°	−6·2°	−6·24°	—	—
B. p.	184° (appx.)	184·40°	184·32—184·39°	—	—
$d_{t°}^{t°}$	1·02315 (20°)	1·03909 (0°)	1·0268 (15°)	1·02479 (17·6°)	1·02840 (12·87°) 1·02225 (21·89°)
$n_D^{20°}$	1·58685	—	1·5850	—	—

The freezing points recorded by other workers are in each case lower than that observed by us. The differences are in our opinion due in all probability to the care we have taken to exclude water. Aniline, like many other organic liquids, takes up small quantities of water with extreme avidity. Our value for the freezing point is confirmed by the work of Ampola (*Gazzetta*, 1895, **27**, i, 35), who obtained — 5·96°, and our value for the refractive index is somewhat supported by the determinations of Brühl and Weegman (compare Landolt-Börnstein, "Tabellen"), both of whom obtained values of $n_D^{20°}$ considerably higher than that of Knowles. The lower freezing point recorded by Knowles would correspond to about 0·1% of water, the refractive index to about 0·7%, assuming the values now obtained to be the correct ones. The various values recorded in the above table for the relative density, though they differ considerably among themselves, lie upon a fairly smooth curve when plotted against the temperature of determination. This is not surprising, since the relative density, while much affected by changes of temperature, is hardly altered by the addition of water as will be shown later.

Density.—Density measurements were made in pyknometers of about 10 c.c. capacity, weighed against sealed counterpoises in the manner described by Hartley and Barrett (J., 1911, **99**, 1072). The pyknometers were filled by slow suction so as to avoid air bubbles, any filling which showed signs of air bubbles or dust being discarded. The filling with aniline occupied about 15 minutes, so that the possibility of absorption of water vapour from the air during filling had to be considered. By filling at rates varying from 10 to 40 minutes, however, no variation of density of the same sample could be detected. It may therefore be assumed that the water absorbed in this time has a negligible effect on the density. Further, careful determinations with a specific gravity bottle, which can be filled much more quickly, gave results in close agreement with the pyknometer determinations. The value obtained for pure aniline was $d_{20°}^{20°} = 1·02315$ or $d_{4°}^{20°} = 1·02136$.

The density of a saturated solution of water in aniline at 20° was found to be $d_{20°}^{20°} = 1·02393$. (The solution used for this determination was prepared in a thermostat, left to settle for several days, and kept at 25° during filling in order to avoid separation of phases.) Thus about 5% of water produces a density-change of only 0·00078.

Refractive Index.—The refractive indices of pure aniline and of some solutions were determined for sodium light by means of a Pulfrich instrument. The liquids were warmed to about 25° and determinations were made during subsequent cooling. The refrac-

tive indices at 20° were read off the resulting refractive index-temperature curves. These curves were all nearly linear, the temperature coefficient in each case being very near to — 0·00030 per degree.

% Water	0·0	1·0484	2·1232	3·0571
$n_D^{20°}$ obs.	1·58685	1·58396	1·58114	1·57861
$n_D^{20°}$ calc.	—	1·58402	1·58112	1·57860

The refractive index is a linear function of the percentage composition, as is seen from the last column, which is calculated from the equation $n_D^{20°} = 1·58685 - 0·00270p$, where p is the percentage of water. The change of refractive index with composition is, however, quite small.

Viscosity.—The viscosities of aniline and of some solutions were measured in three viscosimeters. One, which had a time of flow of about 60 minutes with pure aniline, had been standardised by the method previously described by one of us (J., 1910, **97**, 2000) and found to obey Poiseuille's law accurately. The others, which had times of flow of 45 and 15 minutes respectively, gave the same values for the ratio Time of flow for aniline/Time of flow for water as the standard instrument and therefore were in accord with Poiseuille's law. Using freshly distilled aniline for each determination, values for the time ratio were found varying about a mean value of 4·309. Using Thorpe and Rodger's value for the viscosity of water at 20°, this gives the absolute viscosity of aniline as 0·04468, a value almost identical with that obtained by Poiseuille (0·04467) but considerably higher than the later determinations by Faust (0·433 at 18°) (*Z. physikal. Chem.*, 1912, **79**, 99). No great weight can, however, be attached to these determinations, since it was found that the viscosity of pure aniline is not a constant quantity. The variability of the results obtained and the fact, which further investigation brought to light, that freshly distilled aniline suffers appreciable change in viscosity when kept, even when it is stored in a desiccator in the dark, show that some change takes place after distillation. As an example, aniline kept for a week after distillation had a viscosity of 0·04439, nearly 1% less than that of the freshly distilled sample. The change was not due to absorption of water, since the freezing point showed no depression. The aniline was still fluorescent, though it should be noted that the action of light does produce a further slight change of viscosity.

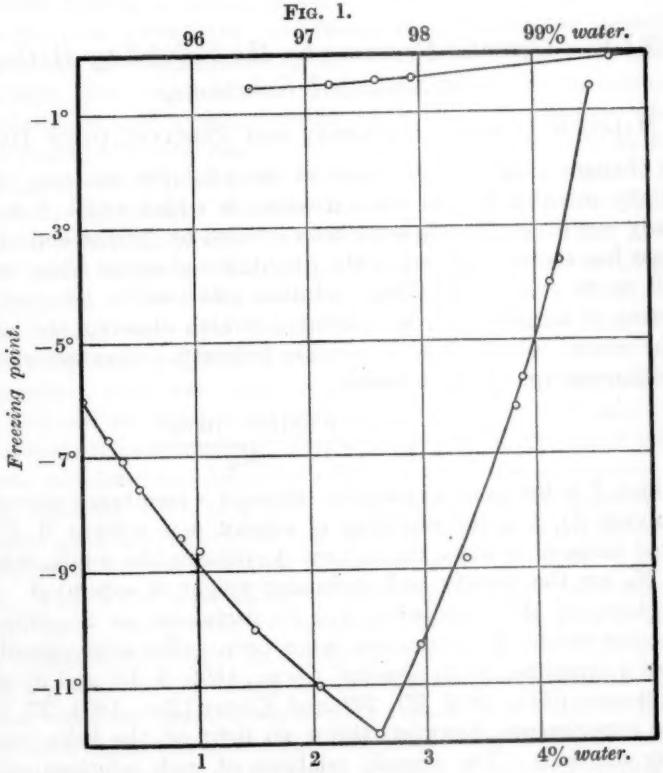
The viscosities of two solutions were measured; they were made up with freshly distilled aniline and gave the following results:—

% Water	0·227	0·344
$\eta^{20°}$	0·0441	0·0438

Freezing Points.—The freezing points were measured in a Beckmann apparatus. The temperatures were in each case determined with different amounts of supercooling, and the accurate freezing points (with no supercooling) estimated from the resulting curve.

% Water.	F. p.	% Water.	F. p.
0	− 5·980°	3·372	−8·80°
0·227	− 6·675	3·820	−6·15
0·344	− 7·050	3·880	−5·65
0·489	− 7·550	4·127	−4·00
0·848	− 8·400	4·219	−3·60
1·015	− 8·625	(congruent	
1·490	−10·000	solutions)	−0·60
2·059	−11·000	97·203	−0·50
2·575 (eutectic)	−11·85	97·608	−0·43
2·952	−10·30	97·928	−0·38

FIG. 1.



The results are plotted in Fig. 1. It will be seen that the eutectic is on the aniline side, the solid separating from solutions containing more than 2·575% of water being ice. The determinations on the ice side of the eutectic were confirmed and extended by Miss E. M. O. Farrow, to whom our best thanks are due. They are necessarily

somewhat uncertain, since in this region a small separation of solid brings about a relatively large change of concentration.

Taking 58·7 as the cryoscopic constant for aniline (Ampola e Rimatori, *Gazzetta*, 1897, **27A**, 35), the calculated molecular weight of water rises from 22·9 in very dilute solution to 25·1 in a solution in the neighbourhood of the eutectic. There is thus clear evidence of association of water in aniline solution. The freezing points of the dilute solutions of aniline in water also indicate association of the solute, the molecular weight calculated being about 105 instead of 93.

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CCXLV.—*Osmotic Pressure by the Solubility Method in Concentrated Solutions.*

By MALCOLM PERCIVAL APPLEBEY and PERCIVAL GLYN DAVIES.

THE changes which are produced in the solubility relations of two partially miscible liquids when a solute is added which is soluble in only one of the liquids have been studied by Nernst and others. Nernst has shown that, when the quantities of solute added are so small as to enable the dilute solution relations to be used, the lowering of solubility of the solvent A (which dissolves the solute) in the second solvent B is an osmotic property, connected with the osmotic pressure by the relation

$$P = \frac{L - L'}{L'} \cdot \frac{0{\cdot}0819T \,.\, 1000d}{M_0}$$

in which P is the osmotic pressure (through a membrane permeable to solvent A), L is the solubility of solvent A in solvent B, L' the altered value of L when the solvent A contains the solute, while d and M_0 are the density and molecular weight of solvent A. The correctness of this expression and its usefulness as a method of molecular-weight determination have been sufficiently proved by Nernst's experiments (*Z. physikal. Chem.*, 1890, **6**, 16) and by those of Tolloczko (*ibid.*, 1896, **20**, 389) and Küster (*Ber.*, 1894, **27**, 324). These experiments, however, throw no light on the behaviour of strong solutions. The osmotic relations of such solutions can at present only be investigated by means of the direct method or by means of vapour-pressure measurements and the application of Porter's relation (*Proc. Roy Soc.*, 1907, **A**, **79**, 519). Of these the direct method is not only costly, but also is only applicable for the very limited range of substances for which a suitable membrane

can be found. The vapour-pressure method, on the other hand, is laborious and also requires for the solution of the integral terms of Porter's equation far more information as to the specific volumes and compressibilities of solution, solvent, and vapour than is usually available. It therefore seemed worth while to investigate the phenomenon of solubility lowering in strong solutions in the hope of opening up another way of approach to the osmotic relations of strong solutions.

The osmotic behaviour of sucrose in aqueous solution has been so much more thoroughly studied than that of any other substance that any experiments on other osmotic properties must begin with this system. The problem of choice of materials accordingly resolves itself into finding a second solvent which can be obtained pure, which dissolves fairly large (and therefore determinable) quantities of water and in which sucrose itself is insoluble. The solvent which best fulfils these requirements is aniline, which may be obtained in a standard and highly purified condition. It dissolves about 5% of water at 20° and has no appreciable solvent effect on sucrose. The aniline, which was obtained from Kahlbaum or Merck, was purified in the manner described in the preceding paper. In all cases, however, the aniline was redistilled not more than 3 days before use. Its purity was frequently tested by determining its freezing point. The freshly distilled aniline froze at $-5{\cdot}98°$; any samples which showed a lower freezing point than $-6{\cdot}1°$ were dried over potash and redistilled.

The water used was twice redistilled from a well-steamed-out glass still and collected in a receiver protected from dust and other atmospheric contamination. The sucrose was Kahlbaum's purest product, powdered and dried in a sulphuric acid desiccator before use.

The solutions were prepared by stirring weighed quantities of aqueous solutions of sucrose of known content with measured quantities of aniline in a mercury-sealed stirring bottle of brown glass. The bottle was immersed in a thermostat maintained at $20° \pm 0{\cdot}01°$. The stirring was continued for a day and the solutions were then left over-night in the thermostat to settle. The aniline phase was removed by means of a dry pipette in experiments where it constituted the upper layer, or by a syphon tube when its density was greater than that of the aqueous phase. In the latter case the difficulty of introducing the syphon without entrapping some of the upper layer was overcome by having the end of the syphon blown out into a thin closed bulb which could be broken against the bottom of the vessel after the syphon was in position. The solutions were then centrifuged in a room the temperature of which never differed by more than a degree from 20°, so as to remove the last

particles of aqueous phase remaining. The method of centrifuging carried out at temperatures differing from the exact experimental temperatures is clearly only permissible when the amount of aqueous phase remaining is negligibly small. It is obvious also that it cannot be used for aniline phases in equilibrium with pure water or very dilute solutions. Other methods have to be used in these cases to obtain complete separation.

Determination of Concentration of Equilibrium Solutions.—It was hoped that some one of the physical properties of aniline might be sufficiently sensitive to the addition of water to enable the composition of solutions to be estimated by careful measurement of the property. Accordingly the variations of density, refractive index, viscosity, and freezing point produced by the addition of water were determined. For one cause or another, all these measurements proved unsuitable. The effect of water on the density and refractive index of aniline is too small; the viscosity is untrustworthy owing to changes occurring with time; and the freezing point is inaccurate as a measure of concentration over the range of the present experiments, since the solid phase separating consists of the component present in small concentration. Details of these measurements will be found in the preceding paper.

In these circumstances recourse was had to direct solubility measurements. Weighed quantities of the solutions, freed from the aqueous phase by centrifuging, were sealed up in glass tubes either alone or with weighed quantities of water added. The tubes were shaken in well-stirred water of slowly changing temperature, and the temperatures at which turbidity occurred on cooling and disappeared on heating were determined. These temperatures differed by not more than 0·2° and the mean was taken to be the temperature of saturation. As there is difficulty in deciding upon a safe criterion of transparency, and as our experience showed that the results depend to a certain extent upon the conditions of lighting of the tubes, it was thought advisable first to construct a solubility curve by measuring the temperatures of saturation of known mixtures of aniline and water, and to use this curve in interpreting our results rather than the determinations of Sidgwick, Pickford, and Wilsdon (J., 1911, **99**, 1122). The following results were obtained, t being the temperature of saturation:

% Water	4·534	4·659	4·815	4·926	4·950	5·398	5·899	6·104
t°	15·9	18·3	20·5	21·15	22·6	34·1	43·5	47·5

A smoothed curve was drawn representing these measurements and used in the subsequent determinations. The saturated solution at 20° from the curve appears to contain 4·835% of water, whereas

Sidgwick, Pickford, and Wilsdon give 5·123%. The discrepancy may be due in part to difference in the aniline used, but is more probably to be ascribed to differences in the conditions of determining the saturation temperatures. It is of no great moment for our purpose, as only comparative measurements are in question. As an example of the consistency of the results obtained in measuring the amount of water in the equilibrium solutions, details are given of the analysis of the aniline phase in equilibrium with a solution of 420 g. of sucrose in 1000 g. of solution.

Wt. of solution (g.).	Water added (g.).	Temp. of satn.	% Water in original soln.
—*	0·0	9·5°	4·57
2·1163	0·0241	39·9	4·53
1·6367	0·0098	27·8	4·56
			Mean 4·55

* The solution in this experiment was not weighed and the temperature was determined in an open tube. The agreement with the other experiments shows that losses during sealing are of no importance.

The method was also tested on two occasions by shaking pure aniline and water in the thermostat at 20°, allowing to stand in the thermostat for a fortnight (the method of centrifuging cannot be used in this case), and determining the temperature of saturation of the aniline layer in unsealed bulbs. The two experiments gave 20·2° and 20·5°, temperatures sufficiently near to 20° to show that the method was satisfactory; if complete separation by centrifuging had been possible, no doubt an even better agreement could have been obtained.

The equilibrium experiments are summarised in the following table:

Conc. of sugar soln.		Conc. of water.		Osmotic press. (atm.).		
g./1000 g. of solution.	g./litre.	g./g. of solution.	Mol. fraction.	From Nernst.	Detd.	Calc.
0	0	0·04835	0·2078	—	7·4	5
300	348·1	0·0466	0·2016	50	40	43
420	498·4	0·0455	0·1976	83	69	67
540	676·1	0·0439	0·1917	135	119	103
660	872·8	0·0407	0·1797	250	218	180

The values for the osmotic pressures in the sixth column are derived from the determinations of Berkeley and Hartley (*Phil. Trans.*, 1906, **206**, A, 481; 1919, **218**, A, 344), allowance being made for the difference of temperature and for the presence of aniline in the aqueous phase.

It will be noted that the Nernst dilute solution formula soon begins to diverge from the experimental values when the concentration becomes fairly large. In the following pages an attempt is

made to relate the solubility lowering to the osmotic pressure of solutions outside the range of the dilute solution law.

Since the two solutions, of sugar in water and of water in aniline, are in equilibrium, they must have the same osmotic pressure through a membrane permeable to water. Now the aniline phase is an extremely concentrated solution of aniline in water of the osmotic pressure of which we know nothing. There is, however, an exact relation between the osmotic pressure of a solution measured by a membrane permeable to one of its constituents and the conjugate osmotic pressure measured by a membrane permeable to the other constituent. This relation, deduced by Berkeley and Burton (*Phil. Mag.*, 1909, **17**, 598), takes the form of a differential equation

$$\frac{dP_1}{dc_2} = \frac{c_2 u_2}{c_1 u_1}\frac{dP_2}{dc_1},$$

in which P_1 = ordinary osmotic pressure–water membrane; P_2 = conjugate osmotic pressure–aniline membrane; c_1 = g. of solvent (water) per g. of solution; c_2 = g. of solute (aniline) per g. of solution; u_1 and u_2 = specific volumes of solvent and solute respectively.

Now the solutions in question, though they are concentrated solutions of aniline in water, are dilute solutions of water in aniline, and it might therefore be supposed that they would obey the dilute solution law $P_2 = RTc_1$ and therefore $dP_2/dc_1 = RT$, in which case Berkeley and Burton's expression can be integrated, giving

$$P_1 = -RT\frac{u_2}{u_1}(\log c_1 + c_2),$$

the constant of integration being zero, since $P_1 = 0$ when $c_2 = 0$ and $c_1 = 1$. This method of interpreting the solubility results was suggested to us by the late Dr. C. V. Burton, and gives at once a value for the osmotic pressures of the sugar solutions. Unfortunately, however, the calculations give results which are widely at variance with the known osmotic pressures of these solutions, and the only conclusion which can be drawn is that the assumption that the conjugate osmotic pressures obey the dilute solution law is very far from being true for saturated solutions of water in aniline. The true value of dP_2/dc_1 must in fact be very much less than RT. The same conclusion may be clearly drawn from many experiments on the freezing points of systems consisting of partially miscible liquids. For example, the curves found by Sidgwick and Turner (J., 1922, **121**, 2257) for the temperatures of separation of *o*- and *m*-chlorophenol in presence of increasing quantities of water bend very definitely upward and appear to meet

the liquid–liquid line almost horizontally, *i.e.*, with a very small value of dT/dc and therefore of dP/dc. The same upward curvature may be observed in the curve for the separation of solid aniline from aqueous solutions (see preceding paper), but not so clearly in this case, since the eutectic intervenes before the curvature has become very pronounced.

Although this method of treatment, in the form suggested by Burton, has proved inadequate to represent the solubility results, it has been found that the application of van Laar's well-known equation for concentrated solutions in place of the dilute solution law gives much more satisfactory results. Assuming that this equation represents the conjugate osmotic pressures, we have $P_2 = -RT \log (1 - c_1) + \alpha c_1^2$. Differentiating and substituting in the Berkeley–Burton equation,

$$\frac{dP_1}{dc_2} = \frac{c_2 u_2}{c_1 u_1}\left(\frac{RT}{1 - c_1} + 2\alpha c_1\right)$$

which, since $c_2 = 1 - c_1$, becomes

$$\frac{dP_1}{dc_2} = \frac{u_2}{u_1}\left(\frac{RT}{1 - c_2} + 2\alpha c_2\right),$$

an expression which on integration gives

$$P_1 = u_2/u_1(-RT \log \overline{1 - c_2} + \alpha c_2^2).$$

(The integration constant is again zero.)

This expression is not without interest, since it shows that if the ordinary osmotic pressure of a solution can be represented by van Laar's expression, so also can the conjugate osmotic pressure, and with the same value for the constant α, which according to van Laar is connected with the mutual attraction of solvent and solute.*

* Mr. D. L. Chapman has pointed out to us that the argument may be put more generally thus. If the product of the osmotic pressure of a solution and the specific volume of the solvent is a function $f(c)$ of its concentration, then the equation of Berkeley and Burton may be written $(1 - c)\frac{df(c)}{dc} = c\frac{df(1 - c)}{d(1 - c)}$, where c is written for c_2 and $1 - c$ for c_1. This is a differential equation which has many solutions, of which, however, the only simple ones are $f(c) = k \cdot \log (1 - c)$ and $f(c) = k'c^2$, k and k' being constants. Putting $k = -RT$ in the first solution, we have van Laar's equation $P = -RT \log (1-c)$, deduced thermodynamically; taking both solutions together and putting $k' = a$, we have van Laar's second expression $P = -RT \log (1 - c) + ac^2$, in which the second term had a somewhat empirical basis. It is of some importance that this second term is now shown to be a solution of the thermodynamic equation of Berkeley and Burton. We may note also that the dilute solution law $P = RTc$ does not satisfy the requirements of this method of deduction, and this law accordingly has no validity except as an approximation to the true law in conditions of extreme dilution.

The application of the new integration to the foregoing solubility results can only be performed in a somewhat approximate manner, since the evaluation of the constant α requires a systematic study of the osmotic pressures of aniline solutions. A preliminary value for α can, however, be obtained by assuming the correctness of the osmotic pressure of a saturated solution of water in aniline, which was calculated (from the lowering of the freezing point) by the usual formulæ as 7·4 atmospheres. The value of R in the expression is not the usual value, since concentrations are expressed in grams per gram of solution, but may be obtained by assuming that a $N/1000$-solution has an osmotic pressure of 0·0224 atm. at 0°; for such a solution the α term is negligible. With the values thus obtained, *viz.*, $R = 4{\cdot}76$, and $\alpha = 4661$, the values tabulated in the last column of the table were obtained. It will be seen that the agreement with the direct determinations of Berkeley and Hartley is fairly satisfactory up to a concentration of 420 g. per 1000 g. of solution, but considerable divergence occurs at higher concentrations. Better agreement can be obtained by adjustment of the constants, but since in any case the osmotic pressure is given as the rather small difference of two large terms, such adjustments have no value except in providing what then becomes a purely empirical equation to express the results.

For the practical determination of osmotic pressures in concentrated solutions the solubility method is not yet capable of giving direct results accurately, though the van Laar integration is a step towards that end. On the other hand, comparative results may be obtained without undue experimental difficulty. By finding the percentage of water in the aniline phase in equilibrium with a solution of unknown osmotic pressure and reading off from our results the concentration of the sucrose solution which is in equilibrium with the same aniline solution we may at once equate the osmotic pressure of the unknown solution to that of the sucrose solution. The method is of course only applicable to solutions of substances the solubility of which in aniline is very slight.

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CCXLVI.—*Studies on the Walden Inversion. Part IX. The Influence of the Solvent on the Sign of the Product in the Conversion of β-Bromo-β-phenylpropionic Acids into β-Hydroxy-β-phenylpropionamides.*

By George Senter and Allan Miles Ward.

In the reaction between concentrated aqueous ammonia and β-bromo-β-phenylpropionic acid, no β-amino-β-phenylpropionic acid is obtained, but the products consist of β-hydroxy-β-phenylpropionamide, styrene, ammonium bromide, and ammonium carbonate (Posner, *Ber.*, 1905, **38**, 2316). The yield of β-hydroxy-β-phenylpropionamide is, however, not good, but is the better the higher the concentration of ammonia employed. These results would lead to the view that this reaction proceeds *via* the corresponding lactone, thus :

$$\underset{\text{(I.)}}{\text{CHBrPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{NH}_4} \xrightarrow{-\text{NH}_4\text{Br}} \underset{\text{(II)}}{\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\text{—O—}} \begin{cases} \rightarrow \text{CHPh:CH}_2 + \text{CO}_2 \\ \rightarrow \underset{\text{(III.)}}{\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2} \end{cases}$$

In the present experiments the reaction of ammonia in ethyl alcohol, in acetonitrile, and also of liquid ammonia with *r*-β-bromo-β-phenylpropionic acid have been investigated, and in each case the hydroxyamide (III) was produced, together with styrene, but no β-amino-β-phenylpropionic acid was isolated. These reactions in non-aqueous solvents are in accordance with the mechanism given above. The reaction of β-bromo-β-phenylpropionic acid with ammonia in dry ethereal solution yields a precipitate of (I), and this appears to be the first salt of this acid to be isolated. It is very unstable, dissolving in water to a clear solution, shortly followed by a pronounced turbidity due to the production of styrene, and decomposing fairly rapidly in the dry state at room temperature, but the lactone (II) could not be isolated from the products of dry decomposition. The *diethylammonium* salt underwent similar decomposition, but with greater ease.

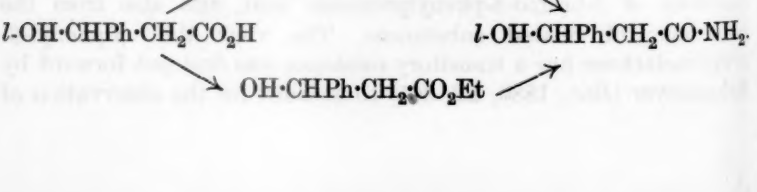
In spite of the failure to isolate the lactone, the mechanism assuming its intermediate formation still seems probable from the reactions of β-bromo-β-phenylpropionic acid, and also from the behaviour of related substances. The view that β-phenyl-β-propionolactone has a transitory existence was first put forward by Erlenmeyer (*Ber.*, 1880, **13**, 305) to account for the observation of

Fittig (*Annalen*, 1879, **195**, 131) that β-bromo-β-phenylpropionic acid reacting with aqueous sodium carbonate yields styrene almost quantitatively. The lactones of all three β-bromo-β-mononitrophenylpropionic acids have been prepared as stable crystalline solids (Einhorn, *Ber.*, 1883, **16**, 2208; Basler, *ibid.*, p. 3001; Prausnitz, *ibid.*, 1884, **17**, 595). The products of decomposition of these lactones by heat, and also by reaction with ammonia, are of the same types as those obtained from β-bromo-β-phenylpropionic acid, the only differences being in the relative proportions of the products.

Not only did liquid ammonia, ethyl-alcoholic ammonia, acetonitrile ammonia and aqueous ammonia solutions yield the hydroxyamide in each case from the *r*-bromo-acid, but with an optically active bromo-acid as initial material, the hydroxyamide produced by reaction in the above solvents was opposite in sign to the bromo-acid used, as shown in the following table:

Solvent.	[α] of bromo-acid.	α of amide.	[α] of amide.
Liquid ammonia	+74·6°	−1·88°	−27·5°
Ethyl alcohol	−75·1	+1·35	+24·3
Acetonitrile	+81·7	−1·93	−28·2
Water	−85·0	+1·68	+27·8

d-β-Hydroxy-β-phenylpropionamide with [α] + 38·4° in ethyl-alcoholic solution has been prepared by McKenzie, Rule, and Martin (J., 1914, **105**, 1588) by the esterification of *d*-β-hydroxy-β-phenylpropionic acid, followed by reaction with ammonia; whilst the *l*-isomeride with [α] − 39·5° was similarly prepared by McKenzie and Smith (J., 1922, **121**, 1359). β-Bromo-β-phenylpropionic acid has not been prepared in a state of optical purity. McKenzie and Humphries (J., 1910, **97**, 121) obtained an acid with $[\alpha]_D$ + 96·2° by recrystallisation of a bromo-acid with $[\alpha]_D$ + 32·2° from chloroform, whilst in the present experiments an acid with $[\alpha]^{13°}$ + 110° for $c = 1·079$, $l = 2$, was obtained as a final crop by fractional precipitation of the bromo-acid from chloroform solution by means of ligroin (b. p. 40—60°). This acid being taken as optically pure, although possibly the activity of the pure acid is somewhat higher, the table shows that very little racemisation accompanies this displacement. Thus by the mode of preparation here adopted, and also in the experiments of McKenzie and his collaborators, the resultant hydroxyamide possesses the same sign as the initial hydroxy-acid, as indicated in the following scheme:



A Walden inversion is not here detected by solvent variation, and the only examples yet obtained of either isomeride being produced in preponderating amount by solvent variation alone is in the single instance in which phenyl and carboxyl are both attached to the asymmetric carbon atom.

EXPERIMENTAL.

β-Bromo-β-phenylpropionic Acids.—The inactive acid was prepared as by Senter and Ward (J., 1924, **125**, 2137), and the active bromo-acids by the conversion of *d*- and *l*-β-hydroxy-β-phenylpropionic acids with hydrogen bromide in glacial acetic acid at 25°, followed by one recrystallisation of the product from chloroform.

Ammonium β-Bromo-β-phenylpropionate.—To 25 c.c. of dry ether previously saturated with ammonia, 2 g. of finely powdered β-bromo-β-phenylpropionic acid were added, and shaken for a few minutes. The solid was washed with dry ether and rapidly dried over concentrated sulphuric acid. The bromine was estimated by heating a weighed sample with aqueous sodium carbonate until styrene was expelled, followed by precipitation as silver bromide (Found: Br, 32·1. $C_9H_{12}O_2NBr$ requires Br, 32·5%). This salt undergoes fairly rapid decomposition in the dry state at room temperature, and rapid decomposition without melting at 60°, the products being ammonium bromide, carbon dioxide, styrene, and a small amount of cinnamic acid.

Diethylammonium β-bromo-β-phenylpropionate was prepared by adding diethylamine (1 mol.) to the bromo-acid (1 mol.) in ethereal solution (2—3%), when white, compact crystals soon commenced to separate. The salt was isolated after 15 minutes as in the case of the ammonium salt, and the bromine estimated in the same way (Found: Br, 26·6. $C_{13}H_{20}O_2NBr$ requires Br, 26·5%). This salt closely resembles the ammonium salt in properties, but is even more unstable, the temperature of rapid decomposition in the dry state being 44—45°.

Conversion of β-Bromo-β-phenylpropionic Acids into β-Hydroxy-β-phenylpropionamides.—The reactions were first carried out with the *r*-bromo-acid, and as in each case β-hydroxy-β-phenylpropionamide resulted (m. p. 121—122°), together with styrene and ammonium bromide as main products, these experiments are not described. The method of experiment with the active acids was as follows: The solvent was added to the bromo-acid (5 g.), and after a definite period the solvent was evaporated on the water-bath (except in 1). The residual solid was extracted with dry ether in a Soxhlet apparatus for 10 hours, and the ether evaporated; the product consisted of crude β-hydroxy-β-phenylpropionamide. The

insoluble residue in the extractor was analysed for bromine in each case; the results are shown under (*a*), the theoretical value for ammonium bromide being Br, 81·6%. Under (*b*) are given the yield of crude hydroxyamide, the observed rotation, the specific rotation, and the percentage of nitrogen (determined by direct distillation into standard acid of the ammonia evolved on decomposition of the amide by heating with excess of aqueous caustic soda). In each case the percentage of nitrogen was appreciably lower than the theoretical (8·5), and the hydroxyamide was markedly acid in reaction. This acidity was removed by shaking a solution of the crude amide in some 125 c.c. of ether with dilute aqueous caustic soda until the aqueous layer was alkaline. The ethereal layer was separated, the alkaline aqueous solution extracted four times with ether, the ethereal solutions were combined, and the solvent was evaporated, when the purified amide remained. Its rotation and analysis are given under (*c*). The remaining aqueous solution in all cases yielded on acidification a small precipitate of cinnamic acid. All measurements of rotation were made in ethyl-alcoholic solution in a 2-dcm. tube with the yellow mercury line.

(1) *Liquid ammonia.* Liquid ammonia (50 c.c.) was added to the *d*-bromo-acid with $[\alpha]^{18^\circ}$ + 74·6°, when a clear solution quickly resulted. This was left in the solid carbon dioxide–ether freezing mixture for ½ hour, when considerable solid had separated. The solvent was then allowed to evaporate.

(*a*) Br, 81·4%.
(*b*) 0·8 g.; α^{16° − 1·69°, *c* = 3·528; $[\alpha]^{16^\circ}$ − 24·0°; N, 8·1%.
(*c*) $\alpha^{22·5^\circ}$ − 1·88°, *c* = 3·422; $[\alpha]^{22·5^\circ}$ − 27·5°; N, 8·3%.

(2) *Ethyl alcohol.* Ethyl alcohol (75 c.c.) at − 15°, dried by distillation over lime and saturated with ammonia at − 14°, was added to the *l*-bromo-acid with $[\alpha]^{15^\circ}$ − 75·1°. The acid rapidly dissolved to a clear solution, and the temperature was allowed to rise slowly. At the end of an hour a considerable precipitate of ammonium carbamate had separated. The solvent was evaporated after 3 hours.

(*a*) Br, 77·5%.
(*b*) 1·6 g.; α^{15° + 1·60°, *c* = 3·644; $[\alpha]^{15^\circ}$ + 22·0°; N, 7·3%.
(*c*) α^{20° + 1·35°, *c* = 2·776; $[\alpha]^{20^\circ}$ + 24·3°; N, 8·2%.

(3) *Acetonitrile.* Acetonitrile (75 c.c.) at − 18°, saturated with ammonia at − 13°, was added to the *d*-bromo-acid with $[\alpha]^{17^\circ}$ + 81·7°. The acid dissolved to a clear solution, from which a heavy precipitate of ammonium bromide rapidly separated. The temperature was allowed to rise slowly, and the solvent was evaporated after 3 hours.

(*a*) Br, 71·1%.
(*b*) 1·4 g.; $\alpha^{16°} - 2·07°$, $c = 3·868$; $[\alpha]^{16°} - 26·8°$; N, 7·8%.
(*c*) $\alpha^{24°} - 1·93°$, $c = 3·422$; $[\alpha]^{24°} - 28·2°$; N, 8·6%.

(4) *Water.* Aqueous ammonia (35 c.c.) saturated at − 10° was added to the *l*-bromo-acid with $[\alpha]^{12°} - 85·0°$, and kept at − 10° for ½ hour. The acid dissolved to a turbid solution and a considerable layer of styrene separated. The solvent was evaporated after 3 hours.

(*a*) Br, 75·9%.
(*b*) 1·3 g.; $\alpha^{15°} + 1·55°$, $c = 3·322$; $[\alpha]^{15°} + 23·3°$; N, 7·4%.
(*c*) $\alpha^{24°} + 1·68°$, $c = 3·028$; $[\alpha]^{24°} + 27·8°$; N, 8·3%.

One of us (A. M. W.) desires to express his indebtedness to the Department of Scientific and Industrial Research for a maintenance grant during the course of this investigation.

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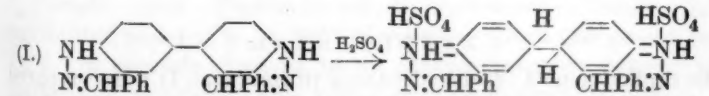
CCXLVII.—*The Colours Produced by the Action of Sulphuric Acid upon Some Hydrazones.*

By FREDERICK DANIEL CHATTAWAY, STANLEY JOHN IRELAND, and ARTHUR JOHN WALKER.

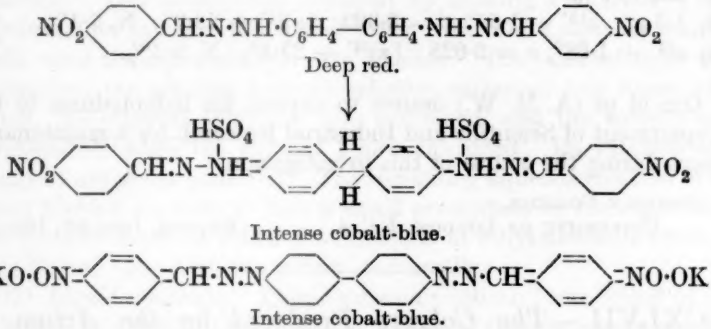
MOST hydrazones when dissolved in strong sulphuric acid give coloured solutions (Bülow, *Annalen*, 1886, **236**, 194; Pechmann, *Ber.*, 1893, **26**, 1045; Troeger and Puttkammer, *J. pr. Chem.*, 1908, **78**, 450). These colours are not as a rule very characteristic, or conspicuous, but those given by many of the hydrazones of diphenylene-4 : 4′-dihydrazine, of *p*-iodophenylhydrazine, and of 4-iodo-2-methylphenylhydrazine are of a peculiarly intense shade of cobalt-blue.

These colours are probably due to the formation of salts of a quinonoid structure similar to that suggested by Wieland (*Ber.*, 1907, **40**, 4260) to account for the brilliant blue colour produced when tetra-*p*-tolylhydrazine is dissolved in sulphuric acid (Chattaway and Ingle, J., 1895, **67**, 1090). For example, in the case of *benzaldehydediphenylene*-4 : 4′-*dihydrazone*, this salt formation may be represented :



Pale yellow. Intense cobalt-blue.

The *hydrazones* which with *o*, *m*, and *p*-nitrobenzaldehyde form these hydrazines are of special interest, for not only do they yield deep blue solutions with strong sulphuric acid, but also in the case of the *o*- and *p*-derivatives give equally characteristic and intense colours with alcoholic potash. These colours also are probably due to the production of salts of a quinonoid structure from the *aci*-form of the nitro-hydrazone. For example, the salts yielded by p-*nitrobenzaldehydediphenylene*-4 : 4′-*dihydrazone* may be formulated thus :



The nitro-group not being concerned in the production of the salt by sulphuric acid, its position scarcely affects the intensity or the character of the colour, all the three isomeric nitrobenzaldehydehydrazones of diphenylene-4 : 4′-dihydrazine, of *p*-iodophenylhydrazine, and of 4-iodo-2-methylphenylhydrazine giving the same intense cobalt-blue.

In the production of colour by alcoholic potash, however, the nitro-group is involved, and, as with other nitrobenzaldehydehydrazones, its character depends on the position occupied by this group. Intense colour is produced only by the *o*- and *p*-isomerides, these alone yielding salts of the necessary quinonoid configuration. The colour produced follows the rule established for *o*-, *m*-, and *p*-nitrobenzaldehydehydrazones in general (Chattaway and Clemo, J., 1923, **123**, 3041), that is, the *o*-nitro-hydrazone gives a bright green, the meta- a brown, and the para- an intense blue colour.

It is worth noting that the colours produced by the *p*-nitrobenzaldehydehydrazones of these hydrazines with sulphuric acid are practically indistinguishable from the intense blue colours which they yield with alcoholic potash.

Experimental.

The diphenylene-4 : 4′-dihydrazones (formulæ as I) were prepared by adding a hot acetic acid solution of the appropriate aldehyde

or ketone (2 mols.) to a hot acetic acid solution of diphenylene-4:4′-dihydrazine (1 mol.). On cooling, the hydrazone separated as a rule as a microcrystalline powder. Nearly all are so sparingly soluble in ordinary organic solvents that they cannot be recrystallised from them. In boiling nitrobenzene, however, they are moderately easily soluble, and separate on cooling in well-developed crystals.

When these hydrazones are added to a large excess of strong sulphuric acid, intensely coloured solutions are produced. In some cases the salts to which the colour is due are comparatively stable and the colours persist at the ordinary temperature for hours or even days with but little change; in others, however, decomposition soon occurs and the colour alters in character or disappears.

After a description of the crystals, the melting point, and the analytical data of the individual hydrazone, the colour produced with strong sulphuric acid is given and then the colour produced by strong alcoholic potash.

Benzaldehydediphenylene-4 : 4′-dihydrazone (I).—Pale yellow needles, m. p. 283° (decomp.) (Found : N, 14·6. $C_{26}H_{22}N_4$ requires N, 14·4%). Brilliant cobalt-blue, which slowly fades, leaving after some hours only a yellowish-brown liquid. It gives no colour with alcoholic potash.

Salicylaldehydediphenylene-4 : 4′-dihydrazone.—Pale yellow plates, m. p. 264° (decomp.). Indigo blue, which on warming, or on long standing becomes green and finally yellow. With alcoholic potash it gives a brownish-yellow solution.

Anisaldehydediphenylene-4 : 4′-dihydrazone.—Pale yellow needles, m. p. 248° (decomp.) (Found : N, 12·4. $C_{28}H_{26}O_2N_4$ requires N, 12·4%). Bright green. With alcoholic potash it gives no colour.

Cinnamaldehydediphenylene-4 : 4′-dihydrazone.—Long, yellow needles, m. p. 253° (decomp.) (Found : N, 12·6. $C_{30}H_{26}N_4$ requires N, 12·7%). Deep sap-green. With alcoholic potash it yields no colour.

Acetophenonediphenylene-4 : 4′-dihydrazone.—Pale yellow, irregular plates, m. p. 250° (decomp.). Heliotrope.

Benzophenonediphenylene-4 : 4′-dihydrazone.—Yellow plates, m. p. 145° (decomp.). Brilliant violet, which soon changes on standing to a dirty, blackish tint.

Pyruvic Acid Diphenylene-4 : 4′-dihydrazone.—Yellow, microcrystalline powder, m. p. 225° (decomp.). Dark orange-red, which in a few seconds changes to an intense magenta colour, which darkens on standing. Pale yellow solution in alcoholic potash.

o-*Nitrobenzaldehydediphenylene*-4 : 4′-*dihydrazone*.—Dark red needles, appearing almost black by reflected light, m. p. 247° (decomp.) (Found : N, 17·6. $C_{26}H_{20}O_4N_6$ requires N, 17·5%). Intense brilliant cobalt-blue indistinguishable in shade from that given by the benzaldehydediphenylenedihydrazone. This colour changes more rapidly than those given by the *m*- and *p*-isomerides, and after 15–20 minutes becomes of a greenish or peacock-blue shade, the green shade becoming more marked as time passes, until after 1–2 hours the liquid is olive-green, which finally becomes yellowish-brown. Deep green solution in warm strong alcoholic potash.

m-*Nitrobenzaldehydediphenylene*-4 : 4′-*dihydrazone*.—Compact, dark red, octahedral crystals, m. p. 257° (decomp.) (Found : N, 17·4%). Intense brilliant cobalt-blue solution indistinguishable from that given by its isomerides. The colour changes less readily that than given by its *o*-isomeride, the peacock-blue shade being developed after about 30 minutes, and changing very little for several hours. Brown solution in alcoholic potash.

p-*Nitrobenzaldehydediphenylene*-4 : 4′-*dihydrazone*.—Deep red, slender plates, m. p. 275° (decomp.) (Found : N, 17·65%). Intense blue solution, indistinguishable in shade from that given by its *o*- and *m*-isomerides, and by benzaldehydediphenylene-4 : 4′-dihydrazone. It dissolves in alcoholic potash giving a brilliant cobalt-blue solution, practically indistinguishable from that given by it and its isomerides with strong sulphuric acid.

Behaviour of the p-*Iodophenylhydrazones with Sulphuric Acid*.—Benzaldehyde-*p*-iodophenylhydrazone dissolves in strong sulphuric acid, giving a deep peacock-blue solution. *o*-, *m*-, and *p*-Nitrobenzaldehyde-*p*-iodophenylhydrazones when added to strong sulphuric acid give at the moment of contact a yellow or orange colour, which very quickly changes to green, and then again rapidly to an intense cobalt-blue, indistinguishable from the colour given by the corresponding diphenylenedihydrazones.

With strong alcoholic potash the benzaldehydehydrazone gives a yellow solution, the *o*-nitrobenzaldehydehydrazone a deep brilliant green, the *m*-nitrobenzaldehydehydrazone a deep clear brown, and the *p*-nitrobenzaldehydehydrazone a brilliant cobalt-blue, indistinguishable from that given with sulphuric acid.

The o-, m-, and p-*nitrobenzaldehyde*-4-*iodo*-2-*methylphenylhydrazones* behave similarly with strong sulphuric acid. A yellow colour momentarily develops, which quickly changes to an intense cobalt-blue. The blue colours are indistinguishable from one another, and from those developed by the corresponding diphenylenedihydrazones.

With strong alcoholic potash similarly the *o*-nitrobenzaldehydehydrazone gives a brilliant green colour, the meta- a clear brown, and the para- a brilliant cobalt-blue, indistinguishable from that given with sulphuric acid.

It is worthy of note that the corresponding hydrazones derived from o- and m-*iodophenylhydrazines* give no intense colours with strong sulphuric acid, only yellow or orange-coloured solutions being obtained. With alcoholic potash, the *o*-nitrobenzaldehydehydrazone gives a deep green, and the *p*-nitrobenzaldehydehydrazone a brilliant cobalt-blue solution.

THE QUEEN'S COLLEGE, OXFORD. [*Received, July 9th,* 1924.]

CCXLVIII.—*Studies in the Camphane Series. Part XL. Constitution of Manasse's Hydroxycamphor.*

By MARTIN ONSLOW FORSTER and PRAJARAM PRABHASHANKER SHUKLA.

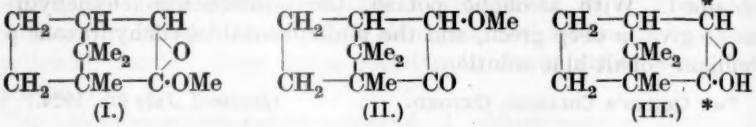
FOLLOWING his initial description of hydroxycamphor (*Ber.*, 1897, **30**, 659), Manasse further characterised the material formed on reducing camphorquinone (*Ber.*, 1902, **35**, 3811) and claimed to recognise two isomeric substances, indistinguishable in appearance and optical activity; the "α"-modification melted at 203—205° with $[\alpha]_D$ 12·8°, whilst the "β"-modification, produced by hydrolysing the solid methyl ether, melted at 212—213° with $[\alpha]_D$ 12·3°.

It is unfortunate that Manasse denominated his materials in this perplexing manner, because it was already known that replacement of hydrogen in the camphor molecule might occur elsewhere than at the α-position; αβ-dibromocamphor, originally called β-dibromocamphor, was first prepared in 1866 by Swarts and reinvestigated many times after 1881, whilst β-bromocamphor was isolated in 1901. Hence, at the time of publishing his experiments, Manasse might well have been aware that a substance called β-hydroxycamphor should correspond in orientation with β-bromocamphor; confusion with the true β-hydroxycamphor subsequently described (Forster and Howard, J., 1913, **103**, 63) might thus have been avoided.

Manasse supported his belief in the existence of two distinct modifications by the production of two oximes, m. p. 86—87° (α) and 83—84° (β), two phenylhydrazones, m. p. 137·5° (α) and 111—113° (β), two semicarbazones, m. p. 182—183° (α) and 202—204° (β) and two benzenesulphonyl derivatives, m. p. 95—96° (α) and 111—113° (β). Excepting the last-named, however, these pairs might have arisen from a single hydroxycamphor, and in view of the

slender distinction between the two parents, one of us (M. O. F.) with Dr. A. Zimmerli began in 1911 an inquiry which was interrupted and could not be resumed until eighteen months ago.

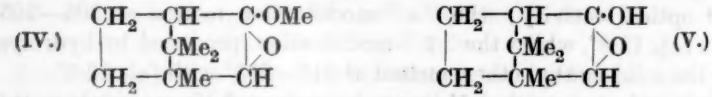
Simultaneous light and shadow have now been cast on the subject by Karrer and Takashima (*Helv. Chim. Acta*, 1925, **8**, 242), who suggest that the solid methyl ether is the *cyclo*acetal (I) and not the true α-methoxycamphor formulated by Manasse (II) :



(I.) (II.) (III.)

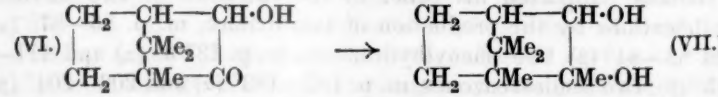
Thereupon they propose for Manasse's α-and β-hydroxycamphors the representation (III), ascribing to configuration-change in one of the asterisked carbon atoms the respective divergence in properties.

Our experiments amply confirm the above suggestion that the solid methyl ether is a *cyclo*acetal, but we cannot support the complete constitutional formula given by Karrer and Takashima. We prefer the alternative representation (IV) with the consequence that Manasse's " β "-hydroxycamphor is the individual (V), whilst his " α "-hydroxycamphor is probably that substance associated with a variable amount of the stereoisomeride in which the hydroxyl group and hydrogen atom both occupy the alternate plane.



(IV.) (V.)

With Karrer and Takashima, we agree that the solid methyl ether does not reveal a carbonyl group; we failed to produce an oxime and recovered the substance unchanged by treatment with magnesium methyl iodide. Moreover, on treating separately (1) the crude product of reducing camphorquinone, (2) " α "-hydroxycamphor, and (3) " β "-hydroxycamphor with excess of the Grignard agent, the quantitative amount of methane required by one hydroxyl group was liberated in each case, and the original product was recovered unchanged. If Manasse's hydroxycamphor had the conventional constitution (VI), it could scarcely escape at least partial conversion into the secondary-tertiary diol (VII), in view



(VI.) (VII.)

of the readiness with which camphorquinone is transformed into the dimethyldiol by magnesium methyl iodide (Forster, J., 1905, **87**, 241).

Our reason for questioning the transference of the hydroxyl group from the true α-position (in V) to the adjacent carbon atom (in III), as represented by Karrer and Takashima, is the one familiar to all chemists who have closely studied the members of this family, namely, the greatly superior activity of the α-carbon atom to that of its ketonic neighbour. The comparative behaviour of camphor and of camphorquinone towards aniline, phenylhydrazine, hydroxylamine, semicarbazide, nitromethane, ethyl cyanoacetate, and phenylacetonitrile may be recalled in this connexion: and finding that Manasse's hydroxycamphor is readily formed by reducing a cold ethereal solution of camphorquinone with aluminium amalgam, we cannot believe that in this reaction alone the diketone has belied itself.

Aside from the question of orientation, however, the above diagnosis by Karrer and Takashima has, in our judgment, clarified a situation which has been hitherto most obscure, and harmonises with the occurrence of Manasse's oximes, phenylhydrazones and semicarbazones, these doubtless arising from cleavage of the ethylene oxide-ring. The two benzenesulphonyl derivatives, to which we have added two hydrogen phthalic esters, are reasonably attributable to the stereoisomeric forms represented by formula V, because, although tertiary alcohols do not generally incur the formation of hydrogen phthalic esters, even limited occurrence of the equilibrium,

would account for the result observed. Moreover, the irregular course of ester-hydrolysis revealed by the polarimeter indicates the operation of concurrent mutarotation in the hydroxycamphor regenerated.

Experimental.

Reduction of Camphorquinone.—(*a*) *Zinc and acetic acid.* Camphorquinone (40 g.) dissolved in hot glacial acetic acid (70 c.c.) was precipitated by hot water (500 c.c.), and zinc dust (40 g.) added in small quantities to the continuously shaken suspension. The clear, pale green liquid was heated to coagulate undissolved zinc, the filtrate from which was saturated with salt and allowed to cool. Hydroxycamphor was removed by filtration; after treating the filtrate with just sufficient sodium hydroxide (20%) to redissolve the zinc hydroxide, more was extracted by ether (three times), in which the separated portion was then dissolved. Dried with calcium chloride, the ether was distilled and left a very pale yellow, camphoraceous residue (32·5 g.; yield 80%).

(*b*) *Aluminium amalgam.* Camphorquinone dissolved in undried ether was left in contact with freshly amalgamated aluminium during 12 hours. The colour faded to very pale green, and the decanted liquid with ether-washings having been dried and distilled deposited a colourless residue (yield 85%).

After crystallisation from petroleum the material prepared by each of the above methods melts at 203—205°; the less readily fusible product described by Manasse has been obtained only by hydrolysing the solid methyl ether. This compound crystallises in colourless plates from a solution of the initial product in methyl alcohol containing hydrogen chloride (6%); it melts at 149—150° (Found: MeO, 15·9. Calc., MeO, 17·0%) and has $[\alpha]_D$ 182·8° (1% in chloroform). The methyl ether is not affected by boiling alcoholic potassium hydroxide (10%), but is rapidly hydrolysed by cold hydrochloric acid, from which sodium carbonate precipitates the less readily fusible form of hydroxycamphor; this melts at 215°, and in all other respects is indistinguishable from the material arising directly on reduction of camphorquinone.

The Hydroxyl Value of Hydroxycamphor. —At one time it seemed possible that the peculiar behaviour of hydroxycamphor might be due to its representing the equilibrium mixture,

but this is now precluded by several indications. In the first place, hydroxycamphor in chloroform does not decolorise bromine, and in ether does not develop a coloration with ferric chloride; moreover, the aqueous solution does not give a precipitate with copper acetate, and the methyl ether is equally indifferent to all these agents. When the action of bromine is pressed by heating hydroxycamphor with the halogen in acetic acid which has dissolved sodium acetate, a very slow action occurs; but this leads to camphoric anhydride without any indication of addition or substitution. The same treatment converts the solid methyl ether also into camphoric anhydride, and in both cases a considerable proportion of unchanged hydroxycamphor is recovered, having survived this attack during several hours.

Conclusive evidence against the above possibility, however, was given by the behaviour of hydroxycamphor towards magnesium methyl iodide, from which the quantitative amount of methane for one hydroxyl group was liberated equally by the crude product of reducing camphorquinone and by specimens of hydroxycamphor melting at 203—205° and at 215°, whilst the methyl ether also

remains unaltered by the Grignard agent without liberating methane. These experiments were conducted in phenetole, and appeared remarkable in view of the observations by Bredt-Savelsberg and others (*J. pr. Chem.*, 1924, **107**, 65) relating to enolisation of camphor by the Grignard agent, which may exceed 40%; but they now receive their explanation in the *cyclo*acetal representation of Karrer and Takashima.

The Camphoryl Hydrogen Phthalates.—A mixture of phthalic anhydride and hydroxycamphor (m. p. 215°) in equal weights, and therefore containing a slight molar excess of the anhydride, was heated at 110—120° during 8 hours and kneaded in a solution of sodium carbonate. On extracting the filtered liquid with ether, about 15% of the hydroxycamphor was recovered unchanged, whilst the hydrogen phthalate was precipitated along with phthalic acid by neutralising the solution of sodium salts; it was separated by dissolution in chloroform, which deposited crystals on evaporation. Recrystallisation from benzene–petroleum gave *camphoryl hydrogen phthalate* in rectangular plates, m. p. 164—165° (Found: C, 68·2; H, 6·6. $C_{18}H_{20}O_5$ requires C, 68·3; H, 6·3%). The $[\alpha]_D$ in aqueous alcohol (1 : 1) was 53·7°.

On repeating this operation with hydroxycamphor melting at 203—205°, or with a specimen recovered unchanged by the methylation process, the proportion of unconverted hydroxycamphor was about the same, and the first crop of crystals melted at 152—156°; this was ultimately resolved into a mixture of the foregoing substance with an isomeric *camphoryl hydrogen phthalate* crystallising in slender needles, m. p. 147° (Found: C, 68·1; H, 6·4%). The $[\alpha]_D$ in aqueous alcohol (1 : 1) was 42·2°.

Thus there appear to be two definite hydrogen phthalates, but it has not been possible to decide whether hydrolysis leads to the respective parents. In fact, on following the hydrolysis polarimetrically, there is an indication of the result being an equilibrium system.

A clear solution prepared by mixing equal volumes of alcohol (97·5%) and aqueous potassium hydroxide (20%) was used. When dissolved in this, the higher-melting hydrogen phthalate passed from the initial $[M]_D$ 102·7° to 61·6° during 200 hours, whilst the isomeride changed from $[M]_D$ 55·0° to 64·4°. Intermediate stages were various, however, the higher-melting form having sunk to $[M]_D$ 60·3° when the isomeride was at 98·6° (after 50 hours), and rising again to $[M]_D$ 73·0° when the isomeride had fallen to 78·3° (after 145 hours). These changes are probably due to varying rates of hydrolysis overlapping unequal mutarotation of the resulting hydroxycamphor, because, in the same alcoholic alkali, higher-melting hydroxycamphor

with initial $[M]_D$ 34·2° reaches a maximum of 82·6° in 26 hours and begins to fall after 48 hours, whilst the lower-melting form has initial $[M]_D$ 50·9°, reaches its maximum of 69·0° at about the same time as the other, and then remains constant. The later observations are only approximate because the liquids, although initially colourless, develop a brown tint which increases in depth with passage of time: moreover, the hydroxycamphor recovered from such solutions melts lower and more indefinitely than the original materials.

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CCXLIX.—*A New Synthesis of Arylazoaldoximes.*

By THOMAS KENNEDY WALKER.

THE interaction of aryldiazonium salts and malonic acid does not always produce formazyl compounds; thus Busch and Wolbring (*J. pr. chem.*, 1905, **71**, 366) obtained phenylhydrazones of glyoxylic acid from certain ortho-substituted diazonium salts and *o*-chlorobenzeneazoformaldoxime from diazotised *o*-chloroaniline, and the present author found (J., 1923, **123**, 2775) that the interaction of diazotised *p*-nitroaniline and allylmalonic acid produced a mixture of a formazyl derivative with an acidic substance the instability of which precluded its examination. As it seemed probable that this anomalous behaviour might be due to the presence of adventitious nitrous acid, a study was made of the simultaneous action of an aryldiazonium salt and nitrous acid on monoalkylated malonic acids. This resulted in a new synthesis of arylazoalkylformaldoximes, *e.g.*, *benzeneazobenzylformaldoxime* and *benzeneazoallylformaldoxime*. The course of the reaction is probably as follows,

$$CHR(CO_2H)_2 + N_2Ph\cdot OH \xrightarrow[-H_2O]{-CO_2} CO_2H\cdot CR{:}N\cdot NHPh \xrightarrow{+HNO_2} OH\cdot N{:}CR\cdot N{:}NPh + CO_2 + H_2O,$$

since an almost quantitative yield of benzeneazobenzylformaldoxime was obtained by the action of nitrous acid on the phenylhydrazone of phenylpyruvic acid, whereas no condensation occurred when diazobenzene was brought into contact with its oxime.

EXPERIMENTAL.

Benzeneazobenzylformaldoxime.—(*a*) To a diazo-solution (aniline 1·86 g., glacial acetic acid 6 g., concentrated hydrochloric acid 6 c.c.; sodium nitrite 1·38 g., ice-water 35 c.c.) were added benzyl-

malonic acid (3·8 g. dissolved in a little ice-water), crystalline sodium acetate (10·8 g.), and, 5 minutes later (this condition is essential for successful preparation), a cooled 2% aqueous solution of nitrous acid (1·5 mols.) The mixture was filtered and kept cold for 30 hours, during which carbon dioxide was evolved. A solution of the bulky, spongy, yellow product in dilute aqueous caustic potash was filtered from a small quantity of benzylformazyl. The *oxime*, precipitated by 5% acetic acid, was crystallised from 80% acetic acid (in small, deep yellow needles) and then from benzene (in paler, silky needles) by the addition of light petroleum; m. p. 144° (yield, nearly quantitative) (Found: C, 70·0; H, 5·4; N, 17·8. $C_{14}H_{13}ON_3$ requires C, 70·3; H, 5·43; N, 17·56%). It is easily soluble in ether, alcohol, chloroform, or ethyl acetate. When boiled with moderately dilute hydrochloric acid, it yields phenylacetaldehyde (which is partly oxidised to the acid), hydroxylamine, and benzenediazonium chloride which, as it is formed, is converted into phenol.

(*b*) A solution of ethyl benzylacetoacetate (14·6 g.) in alcohol (120 c.c.) was mixed at −5° with a solution of diazotised aniline (1 mol.) and the requisite quantity of sodium acetate. The product, which separated as a pale red, viscous oil in quantitative yield after 16 hours, was hydrolysed by warming with 10% aqueous alcoholic caustic potash (3 mols.) for 30 minutes and the solution diluted, filtered, and acidified; the phenylpyruvic acid phenylhydrazone, which separated as an oil and solidified, melting at 161° after recrystallisation (Wislicenus, *Ber.*, 1887, **20**, 592). A solution of the hydrazone in alcohol and 80% acetic acid (equal vols.) was filtered at room temperature and treated with finely-powdered sodium nitrite (3 mols. in one lot); evolution of carbon dioxide occurred. After 30 minutes, when the addition of water to a sample ceased to precipitate any of the original acid, the solution was gradually diluted with cold water. The oxime, which separated in yellow needles (yield quantitative) was recrystallised from benzene–light petroleum; it melted at 144°, alone or mixed with the oxime obtained by method (*a*) (Found: C, 69·9; H, 5·6%).

The *phenylcarbamate*, obtained quantitatively in slender, glistening, orange-red prisms by keeping a mixture of the oxime (3 g.) and phenylcarbimide (1·5 g.) in dry ether (40 c.c.) at 0° for 3 hours, crystallised from acetone in large, scarlet prisms, m. p. 154° (Found: N, 15·8. $C_{21}H_{18}O_2N_4$ requires N, 15·6%). The *benzoyl* derivative, prepared from benzoyl chloride (1 mol.) and the potassium salt of the oxime (1 mol.) in ethereal solution, crystallised from acetone in large, elongated, ruby prisms, m. p. 144—145° (frothing).

p-Tolueneazoallylformaldoxime.—A solution of *p*-toluenediazonium

sulphate (6 g.) in a little ice-water was treated with crystalline sodium acetate (10 g.), followed by a chilled aqueous solution containing allylmalonic acid (4·24 g.) and sodium acetate (7·2 g.). The subsequent addition of nitrous acid and the other operations were carried out as described above under (*a*). The product crystallised from warm benzene in slender, yellow needles, m. p. 93° (shrinking at 90°), and also crystallised well from light petroleum or aqueous alcohol, but not from other solvents. Yield, 25% (Found: C, 65·0; H, 6·5; N, 20·9. $C_{11}H_{13}ON_3$ requires C, 65·0; H, 6·4; N, 20·7%).

Attempts to prepare benzeneazopropaldoxime from ethylmalonic acid by this method resulted only in the production of resinous, uncrystallisable material.

p-*Tolueneazobenzylformaldoxime from Phenylpyruvic Acid* p-*Tolylhydrazone.*—*Ethyl phenylpyruvate* p-*tolylhydrazone*, obtained in nearly quantitative yield from ethyl benzylacetoacetate and *p*-toluidine by the method used in preparing the corresponding phenylhydrazone, crystallises in glistening, orange prisms, m. p. 72° (Found: N, 9·5. $C_{18}H_{20}O_2N_2$ requires N, 9·46%). It is fairly soluble in cold alcohol, more soluble in cold acetone, and very soluble in hot benzene. On hydrolysis, *phenylpyruvic acid* p-*tolylhydrazone* was obtained, which crystallises from alcohol in slender, yellow, felted needles and from acetone in slender prisms, m. p. 158° (frothing). (Found: C, 71·4; H, 6·1. $C_{16}H_{16}O_2N_2$ requires C, 71·5; H, 6·0%).

A solution of this acid (10 g.) in 50 c.c. of 80% acetic acid and 150 c.c. of alcohol was treated with powdered sodium nitrite (3 mols.) and kept for 30 minutes, after which the product was isolated as described above under (*b*). Successive recrystallisations from benzene and from acetone–light petroleum gave the pure *oxime*, m. p. 144° (slight decomp.). Yield, over 80% (Found: C, 70·0; H, 6·1. $C_{15}H_{15}ON_3$ requires C, 70·1; H, 5·9%).

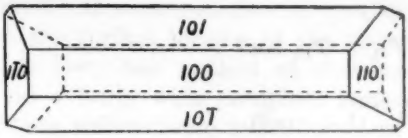
When light petroleum is added to a dilute solution of this oxime in acetone and the liquid allowed to evaporate slowly, the substance separates in transparent, orange-red crystals. Through the kindness of Sir Henry Miers, F.R.S., it has been possible to obtain measurements of these crystals, and the author takes this opportunity of thanking Mr. G. Greenwood, M.Sc., who kindly undertook the crystallographic examination. His report is as follows:—

Crystal symmetry: Monoclinic holohedral.

Axial constants: $a : b : c = 1{\cdot}352 : 1 : 1{\cdot}216$; $\beta = 83° 17'$.

Forms developed and Habit.—The crystals are usually elongated in the direction of the *b* axis and form prisms often 15 mm. long by

about 1·5 mm. thick (see Fig.). The forms present are {100}, {101}, {10$\bar{1}$}, and {110}.



Crystallographic angles.

Angle.	No. of measurements.	Limits.	Mean obs.	Mean calc.
(100) : (101)	11	44° 9′ —44° 30′	44° 20′	—
(100) : (110)	13	53° 9′ —53° 42′	53° 19′	—
(110) : (10$\bar{1}$)	10	67° 55′—68° 34′	68° 18′	—
(100) : (10$\bar{1}$)	17	51° 43′—52° 5′	51° 50′	51° 46′
(110) : (101)	9	64° 30′—65° 7′	64° 49′	64° 42′

The *phenylcarbamate*, obtained quantitatively by keeping a mixture of the oxime and phenylcarbimide (equal mols.) in much dry ether for 2 hours, is difficultly soluble in the usual organic media, but crystallises from much hot acetone in slender, vivid orange-red prisms, m. p. 152—153° (decomp.) (Found : N, 15·1. $C_{22}H_{20}O_2N_4$ requires N, 15·0%).

Benzeneazobenzaldoxime from Phenylglyoxylic Acid Phenylhydrazone.—Ethyl phenylglyoxalate phenylhydrazone was prepared by the general method described above and hydrolysed. The acid, m. p. 163°, obtained could not be converted into the oxime so smoothly as in the other two cases. It proved necessary to keep the mixture cold, avoid excess of sodium nitrite, and work up the product immediately Yield, about 25%.

This work arose out of a previous investigation undertaken at the suggestion of Prof. A. Lapworth, F.R.S., LL.D., to whom the author has pleasure in acknowledging his indebtedness. The author's thanks are also due to the Department of Scientific and Industrial Research for a grant in aid of the work.

THE UNIVERSITY, MANCHESTER. [*Received, October 18th*, 1924.]

CCL.—*Angles of Contact and Polarity of Solid Surfaces.*

By NEIL K. ADAM and GILBERT JESSOP.

IF Dupré's equation

$$W = T_{SV} + T_{LV} - T_{SL} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which relates the free surface energies (surface tensions) at the interfaces of three phases S, V, L, with the work, W, done in separat-

ing S from L across the surface of separation, is combined with the equation of equilibrium of a liquid, L, resting on a solid surface, S, at an angle θ

$$T_{SV} - T_{SL} = T_{LV} \cos\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

we obtain

$$W = T_{LV} (1 + \cos\theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

thus eliminating the quantities T_{SL} and T_{SV} which cannot be determined. Equation (3) has been deduced by Pockels (*Physikal. Z.*, 1914, **15**, 39) and Edser (4th Report on Colloid Chemistry, 1922, p. 310), and an equivalent equation is deducible from Laplace's theory of capillarity (Poincaré, " Capillarité," 1895, 35). It appears to have been very little used. W being the adhesion of the liquid for the solid, and $2T_{LV}$ the cohesion of the liquid, equation (3) shows that zero angle of contact indicates an attraction of liquid for solid at least as great as that of liquid for liquid, 90° shows that this adhesion is half the cohesion of the liquid, and 180° would indicate no adhesion. Clearly measurements of angles of contact against water will give a quantitative measure of the polarity of a solid surface.

We have attempted to use the values of W for solid surfaces of long-chain aliphatic compounds as an indication of the orientation of the surface molecules. If many polar groups are at the free surface, the angle of contact should be low; if the surface consists solely of the hydrocarbon ends of the chains, the angle should be approximately the same as for paraffin wax.

In measuring the angle of contact, we have used a plate of the solid, held in an adjustable holder, which could be set at any angle with the surface, and also raised or lowered by rack and pinion. The water was contained in a glass vessel, preferably rectangular with plate glass sides, filled to the brim; the sides were several millimetres thick and were covered with paraffin on the top; the water surface was cleaned as necessary by scraping with strips of paraffined glass. The plate was set by trial at such an angle that the water surface remained horizontal right up to the edge of the plate, this being determined either by inspection from the side, or by observation of the reflexion of a source of light in the water surface very close to the plate. The angle between the plate and the water surface was then measured by a protractor.

These rather crude arrangements were adequate for this work, as the plates varied in angle of contact, in different parts, by several degrees; there would be little difficulty in improving the optical arrangements, but we would point out that it is of little use to employ accurate optical devices in the measurement of angle of contact

unless both a proper means of obtaining a freshly cleaned water surface and a means of moving the plate relative to the water surface are provided. If contamination is present to an extent sufficient to affect the surface tension of the water, the angle of contact will be too low; the method of cleaning by *paraffined* barriers working on a fairly wide *paraffined* surface at the level of the water has been exhaustively tested in recent work on thin films and found simple and effective. Ablett's most accurate work on paraffin wax (*Phil. Mag.*, 1923, **46**, 244) has probably given a good result, although no means of frequently cleaning the surface was available, because paraffin wax practically does not contaminate a water surface; nevertheless his apparatus would probably not be satisfactory for the majority of substances. An ideal apparatus might combine his method of rotating the cylinder of the solid with the method of cleaning by paraffined barriers.

The principal difficulty in measurement of contact angles is the effect of motion of the solid in dragging the liquid along with it. In extreme cases, the angle when the liquid is advancing over the solid may be 60° greater than when it is receding. It is not necessary that there should be actual motion, for a force on the liquid tending to move it has the same effect. The phenomenon is obvious on inspection of a drop of water on a slightly dirty glass plate; it appears to have been first described in detail by Pockels (*loc. cit.*) and has been accurately measured in one case by Ablett. In the case of some surfaces, when the motion ceases, the line of contact of liquid and solid slips back to give a true equilibrium contact angle, the same whether the motion was advancing or receding. This was only observed with one or two mechanically smooth surfaces, such as a scraped paraffin-wax surface. Ablett's results (on surfaces turned in a lathe) indicate that he obtained a true "stationary" angle of contact. In nearly all cases, including some with paraffin wax, when advancing motion ceased the liquid rose to an angle of contact which was greater than that to which it fell after cessation of receding motion. The angle usually became constant after motion, in less than a minute. So far as our observations go, it is indicated that the rougher the surface is, mechanically, the greater is the difference between the advancing and receding angles; but it is not yet proved that there is always a relation between mechanical roughness and the dragging effect.

The cause of this dragging effect (often called "hysteresis" of the angle of contact) seems to us to lie, not in any absorption of the liquid by the solid, but in a simple friction of the liquid on the surface. Let F be the force of friction which just prevents motion,

then, when the liquid is on the point of advancing, equation (2) becomes

$$T_{SV} - T_{SL} = T_{LV}\cos\theta_A + F \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and when just receding,

$$T_{SV} - T_{SL} = T_{LV}\cos\theta_R - F \quad . \quad . \quad . \quad . \quad . \quad (5)$$

θ_A and θ_R are the angles of contact when the force is just sufficient to move the liquid forwards or backwards, and are therefore the angles measured after moving the plate a short distance and waiting till the angle becomes constant after the motion has ceased.

For the calculation of W by equation (3) the equilibrium angle s required. By adding (4) and (5), and eliminating $T_{SV} - T_{SL}$ by (2),

$$2\cos\theta = \cos\theta_A + \cos\theta_R \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and when (as with the aliphatic substances here considered) the angles are between 45° and 135°, no error greater than 2° arises by substituting

$$2\theta = \theta_A + \theta_R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

By raising the plate of solid vertically by means of the rack and pinion, and taking the mean of the angles after advancing and after receding motion, the following values of the equilibrium angle of contact have been measured. The error is probably of the order 5° in most cases; the angle for a scraped paraffin-wax surface is probably correct to 1°, and agrees with other published determinations.

Surface.	Angle of contact.	Work of adhesion in ergs per sq. cm.
Paraffin wax:		
Scraped surface	105°	54
Solidified in air	105	54
Solidified in contact with water	85 to 100	79·4 to 60·4
Octadecyl iodide:		
Solidified in air	100	60·4
Scraped	95	66·5
Pure hexadecyl alcohol:		
Solidified in air	95	66·5
Scraped surface	50 to 75	123 to 92
Crystal flake	85	79·4
Kahlbaum's "cetyl alcohol" (not crystalline)	20 to 50*	—
Palmitic, stearic, and eicosanic acids, also commercial "stearic":		
Solidified in air	100 to 105	60·4 to 54
Scraped	50 to 105	123 to 54
Crystal flake	95	66
Octadecylamine and eicosylamine hydrochlorides:		
Flakes	45	128

* The "cetyl" alcohol contaminated the water surface very quickly, and possibly the surface tension of the water was lowered sufficiently to render these angles decidedly too low.

There is a strong tendency for the surfaces which have solidified from a melt, in air, to approach the value for paraffin wax. This indicates that the normal orientation of molecules is with the paraffin chains outwards.

Paraffin wax and octadecyl iodide, which contain no groups having a strong affinity for water, give practically the same angle at a surface cut from the interior as at the natural surface. The substances which contain polar groups at one end of the molecule, acids and alcohols, give very varying results for surfaces cut from the interior. These may be as low as 50°, or have practically the same value as the natural surface. It is known from the *X*-ray studies of Müller and Shearer that these substances crystallise in flakes, the unit of which is a layer 2 mols. thick, which has the polar groups in the interior and the hydrocarbon chains outwards. A cut surface which runs parallel to the direction of these flakes in the solid mass will expose very few, if any, polar groups; but one at right angles will expose the maximum number. Hence the variation in the results.

An attempt was made to produce a surface of hexadecyl alcohol containing a very high concentration of polar groups, by solidifying the mass in contact with water, so that the layer of molecules nearest the water might be oriented with polar groups outwards. This was not successful, probably because this outermost layer sticks more closely to the water, to which it is attracted by polar groups, than to the solid plate, to which it is attracted only by the smaller attraction between methyl groups; surfaces crystallised in contact with water were of two kinds, some having a small angle of about 55°, others giving about 100°. Frequently both types of surface were present on the same mass. It was observed that the surface with low angle of contact had a fine structure and did not flake off, the appearance indicating that the crystal flakes were nearly perpendicular to the water; those with high angle easily flaked off, showing that the crystal flakes were parallel to the water.

The table also indicates a tendency of the crystalline flakes (formed from alcoholic or benzene solutions) to have a lower angle of contact than the mass solidified from the melt. The difference is perhaps too small to be trustworthy in the case of the alcohols and acids, but the amine hydrochlorides (which could not be examined after solidification from a melt, as they decompose on melting) gave a very low angle of contact in the flakes. It is very probable, from the similarity of constitution and of the appearance of the flakes, that these flakes have the same molecular structure as those of the acids and alcohols. Thus the very strongly polar groups in the interior *appear* to exercise an appreciable attraction on the

water over a distance equal to the length of an octadecyl chain—about 22 Å.U. Owing to the fact that a layer of closely packed hydrocarbon chains is undoubtedly permeable to water molecules, this cannot be taken as a proof that the attraction of the interior polar groups does actually extend to a distance 22 Å.U., still retaining a considerable fraction of its intensity. The interchange of water between the internal polar groups and the exterior may result in something approaching chains of water molecules in among the hydrocarbon chains, and this would render the exterior surface polar. The flakes of these amine hydrochlorides, immersed in water for some hours, swell, and form a colloidal solution eventually.

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CCLI.—*The Parachor and Chemical Constitution. Part II. Geometrical Isomerides.*

By SAMUEL SUGDEN and HENRY WHITTAKER.

WHILST many physical properties of geometrical isomerides have been investigated and correlated with configuration, no systematic study of the surface tensions of such substances appears to have been made. The work now described was commenced about two years ago with the object of collecting data for pairs of isomerides of known configuration which might provide a basis for a method of determining configuration when the chemical evidence was not conclusive. Meanwhile it was found by one of us (Sugden, J., 1924, **125**, 1178) that the parachor, a quantity involving surface tension and density, can be expressed as a simple additive function of certain atomic and structural constants; from these constants it is possible to calculate the theoretical parachor for all the substances studied and, by comparison of this with the observed figure, to detect the existence of any anomalies.

The determination of the parachor of geometrical isomerides is also of interest, since it has been found (Sugden, Reed, and Wilkins, this vol., p. 1525) that by means of this constant a distinction can be drawn between the two types of double bond which are predicted by the "octet" theory of valency as developed by Lewis, Langmuir, and Lowry. The non-polar double bond, consisting of two covalencies, adds 23·2 units to the parachor, whilst the semipolar double bond, which is made up of one covalency and one electrovalency, lowers the molecular parachor by 1·6 units. It is therefore an easy

matter to determine experimentally the type of linking present in a particular compound. Lowry has suggested that the "activated" molecule of an ethylene derivative may contain a semipolar double bond; this may not, of course, persist in the resting state and Langmuir (*loc. cit.*) assumes that carbon–carbon double bonds are non-polar, so that each carbon atom possesses a complete octet. Further it has been suggested by one of us (Sugden, J., 1923, **123**, 1864), that there must be free rotation about a semipolar double bond; hence it would be expected that compounds which exhibit geometrical isomerism would possess a linking of the non-polar type. It may be stated at once that all the ethylene derivatives so far examined, including those discussed in the present paper, have been found to contain non-polar double bonds.

The substances which have been measured are all methyl esters of unsaturated acids. Esters were used to avoid the complication introduced by association of the free acids, and methyl esters were chosen so that the loading of the molecule, which might obscure small differences between isomeric substances, should be as small as possible.

The results obtained are shown in the accompanying table. Since the calculated value of the parachor includes the effect of a non-polar double bond, the good agreement between the figures in the last two columns shows that all these compounds contain this type of linking. If a semipolar double bond were present the molecular parachor would be 24·8 units lower, and whilst deviations of a few units are present in the observed figures none of them is large enough to suggest the occurrence of this type of bond.

Parachors of cis- *and* trans-*Unsaturated Esters.*

Methyl ester.	Configuration.	Authority.	Parachor. Obs.	Calc.
Cinnamate	trans	Liebermann [1]	373·9	377·9
*allo*Cinnamate	cis	,,	376·1	,,
α-Bromocinnamate	trans	Erlenmeyer [2]	426·6	428·8
α-Bromo*allo*cinnamate	cis	,,	427·9	,,
β-Bromocinnamate	trans	Michael and Brown [3]	424·8	,,
β-Bromo*allo*cinnamate	cis	,, ,,	427·5	,,
Mesaconate	trans	van't Hoff [4]	341·9	347·8
Citraconate	cis	,,	346·1	,,
Fumarate	trans	,,	308·5	308·8
Maleate	cis	,,	309·6	,,

[1] *Ber.*, 1890, **23**, 2511. [2] *Ibid.*, p. 2130. [3] *Ibid.*, 1886, **19**, 1378. [4] "Die Lagerung der Atome im Raume," Braunschweig, 1877, 21.

There is a small but systematic difference between the values of the parachor for each pair of isomerides; the *cis*-compounds, in which two bulky groups are adjacent, give values for the parachor

closely approximating to the theoretical figure, whilst the *trans*-compounds give rather lower values. The difference is small and varies from one unit in the case of maleic and fumaric esters to four units for the mesaconic and citraconic esters. It is therefore little greater than the experimental error; but it appears systematically in each of the pairs of compounds examined, so that configuration does seem to have a real although small effect upon the molecular parachor.

Isomeric substances, *e.g.*, the esters of the formula $C_6H_{12}O_2$ and the three xylenes, have very nearly the same parachor (Sugden, *loc. cit.*, 1180, 1185). Since the atomic constants do not vary in different classes of substances, any differences between the parachors of isomerides must be due to marked differences in structure. The structural constants so far evaluated range from 46·6 for the triple bond to 6·1 for a six-membered ring and appear to depend chiefly upon the degree of unsaturation, or rather upon the crowding of the orbits of shared electrons. The semipolar double bond with a constant of −1·6 fits in with this conception, since, for example, in sulphates and phosphates there is no chemical evidence of unsaturation. Thus a marked difference between the parachors of isomerides would be expected to occur only with a marked difference in structure and in degree of unsaturation, as, for instance, in benzene, for which [*P*] calc. = 207·1, and dipropargyl, for which [*P*] calc. = 224·6. It is therefore not surprising that the configuration of geometrical isomerides has only a small influence upon the molecular parachor.

Experimental.

The isomerides of the cinnamic series were prepared by Sudborough's methods (J., 1903, **83**, 666, 1153). Cinnamic acid was converted into ethyl αβ-dibromo-β-phenylpropionate, the latter treated with alcoholic caustic potash, and the resulting mixture of α-bromocinnamic and α-bromo*allo*cinnamic acids separated by means of the barium salts. Phenylpropiolic acid was prepared by heating bromocinnamic acid with aqueous caustic potash. Sudborough recommends the use of a 20% solution of potash and gently heating on the water-bath, but a better conversion resulted by heating more vigorously with 30% potash. Even under these conditions the reaction was not complete, and difficulty was experienced in the purification of the phenylpropiolic acid until it was found that its barium salt was soluble in dilute ammonia and so could be readily separated from the insoluble barium bromocinnamate. The β-bromo-acids were prepared by the addition of phenylpropiolic acid to saturated aqueous hydrobromic acid, and the isomerides separated by means of their barium salts. *allo*Cinnamic acid was obtained

by reducing β-bromo*allo*cinnamic acid with zinc dust and 96% alcohol; the directions given by Michael (*Ber.*, 1901, **34**, 3651) for the preparation of *iso*cinnamic acid were followed, but the results confirmed the conclusions of Sudborough (*loc. cit.*) that the product is nearly pure *allo*cinnamic acid.

With one exception the methyl esters were prepared from the free acids by the Fischer-Speier method. Maleic acid under this treatment gave a mixture of fumarate and maleate which contained very little maleate; this ester was therefore made by the action of methyl iodide on the silver salt.

The surface tensions of the purified esters were determined by the method of maximum bubble pressure (J., 1922, **121**, 860; 1924, **125**, 27). Seven bubblers were used in the course of the work and in general each substance was measured on two instruments. The constants for these are tabulated below. The densities over a suitable temperature range were determined by means of the

App.	3b.	4a.	4c.	4d.	5b.	6.	6a.
r_1 cm.	0·159	0·139	0·139	0·139	0·140	0·156	0·156
A ...	0·004664	0·003708	0·004790	0·007767	0·009655	0·004439	0·009109

U-shaped pyknometer previously described (J., 1924, **125**, 1171). In the tables below, t is the corrected temperature, P the difference in pressure in dynes/cm.^{2} required to liberate bubbles from the two tubes, D the density in gm./c.c., ϕ the correction factor, and γ the surface tension in dynes/cm. The parachor is calculated by the formula $[P] = \gamma^{1/4}M/D$, where M is the molecular weight.

Methyl cinnamate was recrystallised from ligroin and melted sharply at 33·5° (corr.), M 162·1. Densities determined: 1·078 at 36°, 1·069 at 47°, 1·058 at 61°, 1·046 at 76°, 1·035 at 90°; whence $D^{t}_{4} = 1·107 - 0·000795\ t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4a	46°	9926	1·070	1·010	37·17	374·1
4c	56	7373	1·062	1·0135	35·78	373·4
4a	67	9353	1·053	1·011	35·05	374·4
4c	75	6960	1·047	1·014	33·80	373·4
4a	90	8696	1·035	1·011	32·60	374·3
					Mean	373·9

This substance was measured by Walden and Swinne (*Z. physikal. Chem.*, 1912, **79**, 730) and by Morgan and Chazal (*J. Amer. Chem. Soc.*, 1913, **35**, 1821). They used the density data of Weger (*Annalen*, 1883, **221**, 75), which are 4% lower than ours. Calculated with the aid of our densities, the surface tensions found by Walden and Swinne agree well with our measurements, whilst those of Morgan and Chazal are still low. The latter workers give no criteria by which the purity of their specimen can be judged.

Methyl allo*cinnamate* boiled at 129—130° (corr.)/17 mm., *M* 162·1. Densities determined: 1·088 at 20°, 1·078 at 30°, 1·057 at 51°, 1·047 at 62°, 1·029 at 80°; whence $D_4^t = 1·107 - 0·000977\,t$.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
4d	20°	5069	1·088	1·020	40·17	375·2
,,	41	4732	1·067	1·021	37·53	376·2
,,	62	4400	1·047	1·022	34·93	376·6
,,	78	4139	1·031	1·023	32·88	376·5
					Mean	376·1

Methyl α-*bromocinnamate* boiled at 165° (corr.)/16 mm., *M* 241·0. Densities determined: 1·475 at 20°, 1·450 at 40°, 1·419 at 65°, 1·388 at 90°, 1·363 at 110°, 1·333 at 135°; whence $D_4^t = 1·500 - 0·001238\,t$.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
3b	20°	9618	1·475	1·0165	45·59	424·6
6	30	9828	1·463	1·016	44·32	425·0
3b	51	8810	1·436	1·0175	41·80	426·9
6	61	8966	1·424	1·017	40·47	427·0
3b	81	8044	1·399	1·019	38·22	428·4
4c	112	6948	1·361	1·018	33·87	427·3
,,	131	6469	1·337	1·0195	31·57	427·3
					Mean	426·6

Methyl α-*bromo*allo*cinnamate* boiled at 153·5—154° (corr.)/14 mm., *M* 241·0. Densities determined: 1·450 at 20°, 1·429 at 39°, 1·406 at 57°, 1·397 at 65°, 1·378 at 81°; whence $D_4^t = 1·475 - 0·001195\,t$.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
3b	20°	9155	1·451	1·017	43·41	426·4
6	30	9380	1·439	1·016	42·30	427·3
3b	48	8468	1·417	1·018	40·20	427·4
6	60	8588	1·403	1·017	38·77	428·8
3b	81	7595	1·378	1·0195	36·10	428·8
					Mean	427·9

Methyl β-*bromocinnamate* boiled at 166·5° (corr.)/16 mm., *M* 241·0. Densities determined: 1·468 at 20°, 1·450 at 36°, 1·435 at 49°, 1·411 at 70°, 1·400 at 80°; whence $D_4^t = 1·490 - 0·00113\,t$.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
3b	20°	9445	1·468	1·017	44·79	424·7
4c	32	8706	1·454	1·016	42·36	422·9
,,	53	8263	1·439	1·016	40·21	424·5
6	61	8855	1·421	1·017	39·96	426·5
4c	77	7699	1·404	1·017	37·49	425·0
					Mean	424·8

Methyl β-*bromo*allo*cinnamate* was recrystallised from ligroin and melted sharply at 59° (corr.), *M* 241·0. Densities determined: 1·386 at 62°, 1·376 at 70°, 1·358 at 85°, 1·346 at 95°; whence $D_4^t = 1·461 - 0·00121\,t$.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
6a	66°	3814	1·381	1·038	36·04	427·7
4a	71	9372	1·375	1·014	35·23	427·1
,,	81	9064	1·363	1·014	34·07	427·3
6a	86	3537	1·357	1·041	33·54	427·5
4a	94	8690	1·347	1·015	32·70	427·9
					Mean	427·5

Dimethyl mesaconate boiled at 100° (corr.)/16 mm., *M* 158·1. Densities determined: 1·126 at 20°, 1·115 at 30°, 1·098 at 45°, 1·076 at 65°, 1·060 at 80°; whence $D_4^t = 1·148 - 0·00110t$.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
6a	20°	3691	1·126	1·032	34·68	340·8
4a	32	9010	1·113	1·012	33·80	342·6
6a	52	3268	1·091	1·035	30·80	341·5
4a	63	7945	1·079	1·013	29·84	342·5
6a	80	2928	1·060	1·038	27·68	342·2
					Mean	341·9

Dimethyl citraconate boiled at 103·5° (corr.)/16 mm., *M* 158·1. Densities determined: 1·113 at 26°, 1·101 at 36°, 1·091 at 45°, 1·081 at 55°, 1·070 at 65°, 1·056 at 78°; whence $D_4^t = 1·140 - 0·00108\ t$.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
6a	20°	3801	1·119	1·031	35·69	345·5
4a	32	9208	1·106	1·011	34·51	346·6
6a	53	3332	1·083	1·034	31·37	345·6
4a	64	8203	1·071	1·012	30·78	347·7
6a	79	2986	1·055	1·037	28·20	345·3
					Mean	346·1

Dimethyl fumarate, recrystallised from ligroin, melted sharply at 102° (corr.), *M* 144·1. Densities determined: 1·049 at 106°, 1·032 at 121°, 1·022 at 129°, 1·010 at 140°, 0·999 at 150°, 0·987 at 160°; whence $D_4^t = 1·170 - 0·00114\ t$.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
6a	106°	2708	1·049	1·041	25·67	309·3
,,	123	2503	1·029	1·043	23·77	309·3
4a	132	6040	1·019	1·016	22·75	308·9
6a	146	2221	1·003	1·048	21·20	308·4
4a	163	5083	0·984	1·018	19·18	306·6
					Mean	308·5

Dimethyl maleate boiled at 102° (corr.)/17 mm., *M* 144·1. Densities determined: 1·160 at 20°, 1·144 at 35°, 1·115 at 60°, 1·075 at 95°, 1·058 at 113°, 1·031 at 135°; whence $D_4^t = 1·183 - 0·00112\ t$.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
4c	24°	7682	1·156	1·014	37·31	308·4
5b	35	3642	1·144	1·030	36·21	309·0
4c	51	7020	1·126	1·015	34·12	309·3
5b	67	3239	1·108	1·032	32·26	310·1
4c	86	6150	1·087	1·017	29·95	310·1
,,	113	5509	1·056	1·018	26·85	310·0
,,	143	4795	1·023	1·020	23·42	310·0
					Mean	309·6

Summary.

(1) The surface tension and the density of five pairs of geometrical isomerides have been measured over a range of temperatures.

(2) All the substances examined contain a non-polar double bond adding 23·2 units to the molecular parachor.

(3) The *cis*-compounds, in which two bulky groups are adjacent, have slightly higher parachors than the corresponding *trans*-compounds.

One of us (S. S.) wishes to express his thanks to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of this investigation.

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FETTER LANE, E.C. 4. [*Received, July 9th*, 1925].

CCLII.—*A New Synthesis of Aldehydes.*

By HENRY STEPHEN.

THE basis of this new method is the conversion of a nitrile through the imino-chloride (which need not be isolated) into an aldehyde with the same number of carbon atoms. The most suitable reducing agent is anhydrous stannous chloride * dissolved in ether saturated with hydrogen chloride. Finely powdered, anhydrous stannous chloride (1½ mols.) is suspended in dry ether, which is then saturated with dry hydrogen chloride until the mixture separates into two layers, the lower viscous layer consisting of stannous chloride dissolved in ethereal hydrogen chloride. The nitrile (1 mol.) is now added with vigorous shaking and, after a few minutes, separation begins of a white, crystalline aldimine stannichloride,

$$(R{\cdot}CH{:}NH,HCl)_2,SnCl_4.$$

The course of the formation and reduction of the imino-chloride is therefore as follows: $R{\cdot}CN + HCl \longrightarrow R{\cdot}CCl{:}NH$; $R{\cdot}CCl{:}NH + SnCl_2 + 2HCl \longrightarrow R{\cdot}CH{:}NH,HCl + SnCl_4$. After removal of this

* The anhydrous stannous chloride for these reactions was prepared by heating the crystalline variety until the temperature reached 180°. The product contained some stannous oxide, but this appears to be insoluble in ether saturated with hydrogen chloride. A convenient and rapid method for preparing pure anhydrous stannous chloride is to dissolve the fused mass obtained as above in pyridine. Solution takes place with evolution of heat and the insoluble stannous oxide is then filtered off. The filtrate deposits fine, white needles of a *double* compound, $SnCl_2,2C_5H_5N$ (Found: $SnCl_2$, 53·2; C_5H_5N, 46·4. $SnCl_2,2C_5H_5N$ requires $SnCl_2$, 53·2; C_5H_5N, 46·8%). When the double compound is heated under diminished pressure the pyridine is removed; the residue is anhydrous stannous chloride.

salt the ether may be again employed for another preparation. The salt is readily hydrolysed by warm water, and the aldehyde formed may be removed by distillation with steam or extraction with a solvent.

The method is applicable to aliphatic and aromatic nitriles, and the yields are usually almost quantitative. As the rate of deposition of the stannichloride varies in different cases, it is advantageous to allow at least two hours for completion of the reaction.

3 : 4 : 5-Trimethoxybenzonitrile and other nitriles which are only sparingly soluble in cold ether may be dissolved in chloroform and the solution added to the reducing agent.

o-Toluonitrile and α-naphthonitrile give only small yields of the respective aldehydes. This is no doubt due to steric hindrance, of which the two nitriles form well-known examples; both, for instance, fail to give imino-ethers (Pinner, "Die Imidoäther und ihre Derivate," 1892, pp. 4, 81), for the formation of which an imino-chloride is essential.

A special application of the method is the formation of indole by reduction of *o*-nitrophenylacetonitrile; sufficient reducing agent is employed to reduce both the imino-chloride and the nitro-group:

$$C_6H_4\langle^{CH_2\cdot CN}_{NO_2} \rightarrow C_6H_4\langle^{CH_2\cdot CHO}_{NH_2} \rightarrow C_6H_4\langle^{CH}_{NH}\rangle CH$$

(compare Pschorr, *Ber.*, 1910, **43**, 2543).

Experimental.

n-*Octaldehyde*.—Octonitrile was prepared by warming a solution of octoamide in thionyl chloride on the water-bath for 30 minutes and removing the excess of thionyl chloride under diminished pressure. The residue of nitrile (b. p. 87°/10 mm.) was almost pure and the yield quantitative. The method has been applied to the amides of myristic, palmitic, and stearic acids with equally good results.

Octonitrile (25 g.) was brought into reaction with stannous chloride (57 g.) in dry ether (200 c.c.), saturated with hydrogen chloride as described above. The aldehyde produced by hydrolysis of the stannichloride was isolated by distillation with steam and extraction with ether. It was obtained as a colourless oil, b. p. 65°/11 mm., having a strong lemon-like odour. Prepared by the usual methods and crystallised from methyl alcohol, the oxime was obtained in fine, silky needles, m. p. 60°, the semicarbazone in needles, m. p. 98°, and the p-*nitrophenylhydrazone* in bright yellow needles, m. p. 80° (Found: N, 15·8. $C_{14}H_{21}O_2N_3$ requires N, 15·9%).

Myristaldehyde was prepared from the corresponding nitrile, but being only slightly volatile in steam it was extracted with warm ether after hydrolysis of the stannichloride. It was obtained as thin, colourless laminæ, m. p. 23°, b. p. 155°/10 mm., and rapidly polymerised to a white solid, m. p. 65°. The oxime and semicarbazone crystallised from methyl alcohol in needles, m. p. 82·5° and 106·5°, respectively (compare Le Sueur, J., 1905, **87**, 1900). The p-*nitrophenylhydrazone* is a bright yellow, crystalline powder, m. p. 95° (Found: N, 12·4. $C_{20}H_{33}O_2N_3$ requires N, 12·1%).

Palmitaldehyde formed thin plates with nacreous lustre (from ether), m. p. 34°; the polymeride had m. p. 73—74°. The oxime and semicarbazone crystallised from methyl alcohol in needles, m. p. 88° and 107°, respectively (Le Sueur, *loc. cit.*). The p-*nitrophenylhydrazone* formed yellow needles, m. p. 96·5°, from alcohol (Found: N, 11·3. $C_{22}H_{37}O_2N_3$ requires N, 11·2%).

Stearaldehyde has m. p. 38°, not 63·5° as stated by Krafft (*Ber.*, 1880, **13**, 1417). It rapidly polymerises to a white solid, m. p. 80° The oxime and semicarbazone crystallise in needles, m. p. 89° and 108—109°, respectively. The p-*nitrophenylhydrazone* forms yellow needles, m. p. 101°, from methyl alcohol (Found: N, 10·6. $C_{24}H_{41}O_2N_3$ requires N, 10·4%).

Benzaldehyde.—Benzonitrile is rapidly and almost quantitatively converted into benzaldehyde by the new method. The *stannichloride* was obtained in white needles from alcohol (Found: Sn, 21·2. $C_{14}H_{16}N_2Cl_6Sn$ requires Sn, 21·8%). The salt, if dry, may be preserved indefinitely. It dissolves in water, but is rapidly hydrolysed when the solution is warmed.

3 : 4 : 5-*Trimethoxybenzaldehyde.*—The corresponding nitrile is readily obtained by the action of thionyl chloride on the amide (yield 90%), and without further purification melts at 93° as stated by Harding (J., 1911, **99**, 1594). A solution of the nitrile (9 g.) in 20 c.c. of chloroform is added to anhydrous stannous chloride (9 g.) in ether (150 c.c.) saturated with hydrogen chloride. After an hour the yellow stannichloride is filtered off, hydrolysed by boiling water, and the solution filtered. 3 : 4 : 5-Trimethoxybenzaldehyde crystallises from the filtrate in shimmering leaves, m. p. 74—75°. The oxime has m. p. 88°; the semicarbazone, m. p. 218°; and the *p*-nitrophenylhydrazone, m. p. 201° (compare Mauthner, *Ber.*, 1908, **41**, 923).

Indole.—*o*-Nitrophenylacetonitrile (3 g.) is added to a solution of anhydrous stannous chloride (16 g.) in ether (100 c.c.) saturated with hydrogen chloride. After remaining 2 hours, the stannichloride is filtered off, dissolved in water, the solution made alkaline with sodium hydroxide, and the indole removed in a current of

steam. The product, m. p. 52° (yield 1·2 g.), shows all the characteristic properties of indole.

The following aldehydes have been prepared by the new method, and except in the cases marked * the yields were almost quantitative. *o*-Tolualdehyde,* b. p. 94°/10 mm.; p-*nitrophenylhydrazone*, red needles, m. p. 222°, from alcohol (Found : N, 16·2. $C_{14}H_{13}O_2N_3$ requires N, 16.4%). *p*-Tolualdehyde, b. p. 106°/10 mm.; p-*nitrophenylhydrazone*, similar to the above, m. p. 200·5° (Found : N, 16·5%). *o*- and *p*-Chlorobenzaldehydes, phenyl-, *p*-chlorophenyl-, and *p*-tolyl-acetaldehydes (p-*nitrophenylhydrazone* of the last, yellow needles from alcohol, m. p. 144·5°. Found : N, 15·3. $C_{15}H_{15}O_2N_3$ requires N, 15·6%), cinnamaldehyde and β-phenylpropaldehyde, α-naphthaldehyde * (m. p. 33—34°; oxime, m. p. 39°; semicarbazone, m. p. 222°; p-*nitrophenylhydrazone*, orange needles, m. p. 234°. Found : N, 14·4. $C_{17}H_{13}O_2N_3$ requires N, 14·4%). The investigation is being continued.

In conclusion, the author has to thank Professors Lapworth and Robinson for their interest in the research.

THE UNIVERSITY, MANCHESTER. [*Received, June 26th*, 1925.]

CCLIII.—*ββ′-Dichloro- and ββ′-Dibromo-diethyl Selenides and their Simple Halogen Derivatives.*

By HUGH CHESTER BELL and CHARLES STANLEY GIBSON.

IN studying the reaction between ethylene and selenium monochloride, Bausor, Gibson, and Pope (J., 1920, **117**, 1453) showed that ββ′-dichlorodiethyl selenide dichloride (m. p. 122·5°) is formed and that the reaction proceeds according to the equation $2CH_2{:}CH_2 + 2Se_2Cl_2 = (CH_2Cl{\cdot}CH_2)_2SeCl_2 + 3Se$. Heath and Semon (*Ind. Eng. Chem.*, 1920, **12**, 1100) suggested that the final product is *s*-tetrachlorodiethyl selenide, $(CHCl_2{\cdot}CH_2)_2Se$, m. p. 118°.† On the other hand, Boord and Cope (*J. Amer. Chem. Soc.*, 1922, **44**, 395) agree that the final product is ββ′-dichlorodiethyl selenide dichloride, but they advance arguments to prove that the reaction goes in two stages :

(*a*) $2C_2H_4 + Se_2Cl_2 = (C_2H_4Cl)_2Se + Se$.
(*b*) $(C_2H_4Cl)_2Se + Se_2Cl_2 = (C_2H_4Cl)_2SeCl_2 + 2Se$.

In their paper Boord and Cope do not give any indication that they have investigated the reaction between ethylene and selenium

† These authors state that hydrogen chloride is evolved during the reaction. We have found that this is not so if precautions are taken to exclude moisture.

monochloride and did not isolate ββ′-dichlorodiethyl selenide which, the present work has further proved, was described by Bausor, Gibson, and Pope for the first time (compare Boord, *Ind. Eng. Chem.*, 1919, **11**, 101). The argument advanced by Boord and Cope is based on the results of experiments on the reaction between selenium monochloride and propylene, butylene, and amylene, respectively, and they show in each case that when selenium monochloride is added to the olefine the ββ′-dichlorodialkyl selenide is produced (reaction *a*). The only case of the formation of a selenide dichloride found by Boord and Cope was when they carried out the reaction between selenium monochloride and propylene, substantially under the conditions maintained by Bausor, Gibson, and Pope in the case of ethylene, and they obtained ββ′-dichlorodipropyl selenide dichloride. If the reaction between the olefines and selenium monochloride is a general one and occurs in two stages as stated by Boord and Cope, then that between the selenide and selenium monochloride (*b*) must be quantitative and proceed under the ordinary conditions of the experiment. In only one case apparently did the authors try this; they found that when equimolecular quantities of selenium monochloride and ββ′-dichlorodibutyl selenide were mixed the selenide dichloride was not obtained. The work of Boord and Cope indicates that the selenide dichlorides from butylene and amylene are difficult to prepare and may not have been obtained, but it affords little evidence that the reaction between ethylene and selenium monochloride takes place in two stages.

When selenium monochloride in chloroform is added to a chloroform solution of ββ′-dichlorodiethyl selenide at the ordinary temperature the formation of ββ′-dichlorodiethyl selenide dichloride is, we find, instantaneous and selenium separates at once. Although it may be convenient to regard the formation of the selenide as a phase in the reaction, it is clear that it cannot exist in the presence of selenium monochloride for any appreciable time. We describe below a highly satisfactory method for the preparation of ββ′-dichlorodiethyl selenide from the dichloride in which the possibility of its contamination with selenium is avoided and since the preparation of the dichloride can be carried out so readily we have not investigated the possibility of the preparation of the somewhat toxic selenide directly from selenium monochloride which, at the best, would involve the separation of the product from selenium.

ββ′-Dichlorodiethyl selenide dichloride can be prepared not only by the action of ethylene on selenium monochloride, but also in quantitative yield from selenium tetrachloride,

$$2C_2H_4+SeCl_4=(CH_2Cl\cdot CH_2)_2SeCl_2,$$

and the separation of the product from selenium is thereby avoided. It is possible to chlorinate selenium in the presence of benzene (very little chlorination of the latter takes place) or other suitable solvents to the tetrachloride and to convert this quantitatively into the final product, the same vessel being used throughout. In an analogous manner, ββ′-*dibromodiethyl selenide dibromide* is obtained, starting with selenium.

Bausor, Gibson, and Pope suggested that the colourless, crystalline substance, m. p. 23—25°, obtained in small quantity by reducing a cold aqueous solution of ββ′-dichlorodiethyl selenide dichloride with sulphur dioxide is probably ββ′-dichlorodiethyl selenide (*loc. cit.*). This is the fact. It can also be prepared by reducing the dichloride with hydrogen sulphide or, best, with potassium metabisulphite. It has a characteristic and persistent garlic-like odour and its toxicity appears to be very much less than that of ββ′-dichlorodiethyl sulphide. The corresponding ββ′-*dibromodiethyl selenide* is prepared in an analogous manner by reduction of the corresponding dibromide.

On treatment under appropriate conditions with either chlorine or bromine, the selenides combine with two atomic props. of the halogen. Apart from the dichloride and the dibromide already mentioned, we have prepared in this way ββ′-*dichlorodiethyl selenide dibromide* and ββ′-*dibromodiethyl selenide dichloride*. Since chlorine combines with ββ′-dichlorodiethyl selenide to give the product obtained by the reaction of ethylene with selenium monochloride, these compounds afford additional evidence of the correctness of the constitution given to ββ′-dichlorodiethyl selenide dichloride by Bausor, Gibson, and Pope. ββ′-Dichlorodiethyl selenide dichloride is precipitated from its aqueous solution by hydrochloric acid, and similarly the corresponding dibromide is precipitated by hydrobromic acid. The product obtained by adding hydrochloric acid to an aqueous solution of ββ′-dibromodiethyl selenide dibromide was proved to be the dichloride by its yielding ββ′-dibromodiethyl selenide on reduction with potassium metabisulphite. Under similar conditions, ββ′-dichlorodiethyl selenide dibromide is converted into ββ′-dichlorodiethyl selenide. It is interesting to compare the instability of ββ′-dichlorodiethyl sulphide dibromide (Gibson and Pope, J., 1920, **117**, 277) with the great stability of the analogous compounds of selenium now described.*

* Propylene reacts with selenium tetrachloride in a precisely similar manner to ethylene, and a quantitative yield of ββ′-dichlorodipropyl selenide dichloride results. This compound, reduced by potassium metabisulphite, is converted quantitatively into ββ′-dichlorodipropyl selenide (compare Boord and Cope, *loc. cit.*).

So far, all attempts to prepare direct oxidation products of ββ′-dichlorodiethyl selenide have failed. Although part of it is destroyed in the process, ββ′-dichlorodiethyl selenide dichloride can be recrystallised from concentrated nitric acid. Under the conditions for converting ββ′-dichlorodiethyl sulphide into the corresponding sulphoxide (Gibson and Pope, *loc. cit.*), ββ′-dichlorodiethyl selenide is partly destroyed and the dichloride crystallises out from the solution. Although the dichloride in aqueous solution behaves like the chloride of a bivalent metal, we have not been able to isolate either the corresponding hydroxide or oxide. An attempt to prepare the oxide by the action of ethylene on selenium oxychloride resulted in the formation of the dichloride and selenium dioxide, the following reaction presumably taking place :

$$2SeOCl_2+2C_2H_4=SeO_2+(C_2H_4Cl)_2SeCl_2.$$

Experimental.

ββ′-Dichlorodiethyl Selenide Dichloride.—Some quantity of this compound was prepared by the original method from selenium monochloride and the previous results were confirmed in all respects. When an excess of dry ethylene was passed into a dry benzene solution of selenium monochloride, hydrogen chloride was not evolved for the issuing gas produced no change in the alkalinity of standard sodium hydroxide. In an actual experiment, dry ethylene was passed into a rapidly stirred solution of 42 g. of selenium monochloride in dry benzene, cooled in running water. The yields of ββ′-dichlorodiethyl selenide dichloride and of precipitated selenium obtained were 24 g. and 19 g., respectively; according to the equation, they should be 25·4 g. and 21·7 g.

The preparation from selenium tetrachloride is, however, much more convenient, since all contamination with selenium is avoided. A rapid stream of chlorine is passed into a cooled, well-stirred suspension of finely divided selenium (1 part) in a convenient amount of benzene (carbon tetrachloride, chloroform or ether may be used). Selenium tetrachloride is formed with evolution of heat and separates rapidly as a pale yellow powder. The chlorine supply is then cut off, finely divided selenium (3 parts) added, and stirring continued for some time, during which the selenium tetrachloride is converted into the monochloride and almost complete solution is effected. The somewhat diluted benzene solution is filtered in a dry atmosphere, and chlorination is continued rapidly under the same conditions as before until the solution is completely decolorised and the selenium tetrachloride separates as a pale yellow powder, almost insoluble in most organic solvents. After

freeing the solution from excess of chlorine by passing dry air, ethylene is passed in until complete solution of the selenium tetrachloride is effected in the warm solvent, which should become quite colourless when the reaction is finished. The dichloride crystallises as the solution cools and the small amount remaining in solution can be recovered in the usual manner. In this way, from a total amount of 20 g. of selenium, 60—65 g. of ββ′-dichlorodiethyl selenide dichloride can be prepared conveniently in the course of about 8 hours including the preparation of the necessary ethylene. That the reaction between selenium tetrachloride and ethylene takes place according to the equation $2C_2H_4+SeCl_4=(C_2H_4Cl)_2SeCl_2$ was proved by passing ethylene into dry benzene in which 10 g. of the tetrachloride was suspended. Twelve grams of the resulting compound was obtained (theory requires 12·5 g.).

The identity of the compound prepared from selenium tetrachloride with that prepared from the monochloride was proved by its melting point (122·5°), by its crystalline form, and by its behaviour with sodium hydroxide in cold aqueous solution (Found: titratable Cl, 25·9; *M*, cryoscopic in hexachloroethane,* 276. Calc. for $C_4H_8Cl_4Se$: titratable Cl, 25·6%; *M*, 277·2). The compound is best purified by recrystallisation from chloroform. It can be almost quantitatively recovered from its aqueous solution by addition of concentrated hydrochloric acid and this is also a convenient method of purification. Its aqueous solution decomposes above 35°, and rapidly when boiled, with evolution of ethylene.

When concentrated hydrobromic acid was added to a cold aqueous solution of ββ′-dichlorodiethyl selenide dichloride, a yellow, crystalline precipitate was obtained which, after recrystallisation from chloroform, had m. p. 117° (decomp.) and was proved by its constants and by analysis to be ββ′-*dichlorodiethyl selenide dibromide*, obtained also in another way (see p. 1883).

In attempts to isolate ββ′-dichlorodiethyl selenide dihydroxide, careful addition of sodium hydroxide (2 equivs.) to the aqueous solution of the dichloride gave negative results. Similarly, in attempting to prepare ββ′-dichlorodiethyl selenide oxide by the action of dry silver oxide on a benzene solution of the dichloride, selenium was deposited and no oxide-like substance could be isolated.

ββ′-*Dibromodiethyl Selenide Dibromide*, $(CH_2Br\cdot CH_2)_2SeBr_2$, is prepared in an analogous manner to the dichloride. Finely divided selenium is suspended in pure carbon tetrachloride and bromine is added to the rapidly stirred suspension until the whole of the

* The use of hexachloroethane for the determination of molecular weights has not yet been described but, as soon as its general applicability has been determined, an account will be submitted for publication.

bromine is converted into the tetrabromide. The excess of bromine is removed either by boiling or by passing a current of dry air. Dry ethylene is then passed into the rapidly stirred suspension of the tetrabromide until the solution becomes clear; the ββ′-dibromodiethyl selenide dibromide dissolves in the warm solvent and crystallises on cooling. One crystallisation from chloroform is sufficient for complete purification, well-formed, bright yellow prisms, m. p. 118°, being obtained (Found : Br, 71·1. $C_4H_8Br_4Se$ requires Br, 71·6%).

ββ′-*Dichlorodiethyl Selenide*, $(CH_2Cl{\cdot}CH_2)_2Se$.—The substance, m. p. 23—25°, originally prepared by Bausor, Gibson, and Pope (*loc. cit.*) by passing sulphur dioxide into a cold aqueous solution of ββ′-dichlorodiethyl selenide dichloride, was prepared again by the same method and proved to be ββ′-dichlorodiethyl selenide identical with the product obtained more conveniently by a slightly different procedure.

ββ′-Dichlorodiethyl selenide dichloride may be reduced in boiling benzene solution by dry hydrogen sulphide. Sulphur separates and the reaction is finished when hydrogen chloride ceases to be evolved. On distilling off the benzene from the filtered solution, a product is obtained, m. p. about 24°, which is extremely difficult to obtain free from adhering sulphur. On extraction with dry ether, some sulphur is left undissolved, but the melting point of the product is scarcely affected. Fractional freezing of the material to free it from sulphur is not very satisfactory and even after repeating this process several times analysis shows that the resulting material is not quite pure (Found : Cl, 33·2%).

After many experiments the following method was finally adopted for preparing ββ′-dichlorodiethyl selenide conveniently in a state of purity. A solution of pure ββ′-dichlorodiethyl selenide dichloride (10—15 g.) in cold water is shaken with cold aqueous potassium metabisulphite (calc. quantity) and at once extracted with ether. The ethereal solution is washed with water, dried with calcium chloride, and evaporated; the selenide crystallises easily (yield almost theoretical). It is convenient to purify it by pressing on to clean unglazed porcelain and subsequent fractional freezing. It crystallises in colourless needles, m. p. 24·2° (Found : Cl, 34·7; Se, 38·6; *M*, cryoscopic in benzene, 196. Calc. for $C_4H_8Cl_2Se$: Cl, 34·4; Se, 38·4% : *M*, 206). Unlike the corresponding sulphide, it cannot be distilled in a water-pump vacuum without considerable decomposition. The distillate, however, contains some unchanged selenide which is identified by conversion into the dibromide (see below).

ββ′-Dichlorodiethyl selenide combines with chlorine (1 mol.) to

give the dichloride and with bromine (1 mol.) in chloroform solution. The reaction is quantitative: 0·3915 g. decolorised 0·315 g. bromine, the theoretical quantity being 0·303 g. bromine. The compound so formed is therefore ββ′-*dichlorodiethyl selenide dibromide*, $(C_2H_4Cl)_2SeBr_2$, which crystallises from chloroform in pale yellow prisms, m. p. 117° (decomp.). This compound, on reduction with potassium metabisulphite in the manner already described, yields ββ′-dichlorodiethyl selenide. It has been mentioned that when hydrobromic acid is added to a cold aqueous solution of ββ′-dichlorodiethyl selenide dichloride this dibromide is precipitated (see p. 1881) and the facts now brought forward prove that when ββ′-dichlorodiethyl selenide dichloride is dissolved in water the halogen atoms attached to the selenium are hydrolysed.

When a chloroform solution of selenium monochloride is added to a similar solution of ββ′-dichlorodiethyl selenide, selenium is at once precipitated and the filtered solution yields a quantitative amount of ββ′-dichlorodiethyl selenide dichloride. The reaction takes place with evolution of heat and proceeds according to the equation $Se_2Cl_2+(C_2H_4Cl)_2Se=(C_2H_4Cl)_2SeCl_2+2Se$.

When ββ′-dichlorodiethyl selenide is oxidised with nitric acid, the only product which has up to the present been isolated is ββ′-dichlorodiethyl selenide dichloride (identified by its melting point and crystalline form), part of the selenide being destroyed. An attempt to prepare the oxide by the action of ethylene on selenium oxychloride resulted in the formation of selenium dioxide and ββ′-dichlorodiethyl selenide dichloride, the selenium oxychloride reacting as an equimolecular mixture of selenium dioxide and selenium tetrachloride.

ββ′-*Dibromodiethyl Selenide*, $(CH_2Br{\cdot}CH_2)_2Se$.—This compound is prepared by reduction of ββ′-dibromodiethyl selenide dibromide by means of potassium metabisulphite under the conditions already described. It crystallises from ethyl alcohol in yellow needles, m. p. 44·2°, and is much more easily handled than the corresponding chloro-compound (Found: Br, 53·5. $C_4H_8Br_2Se$ requires Br, 54·2%).

It combines with chlorine in chloroform solution to give ββ′-*dibromodiethyl selenide dichloride*, $(C_2H_4Br)_2SeCl_2$, pale yellow prisms, m. p. 98—99°, from chloroform (Found: Cl+Br, 62·8. $C_4H_8Cl_2Br_2Se$ requires Cl+Br, 63·0%). This compound has a greater solubility in organic solvents than the analogous compounds already mentioned. The same compound is precipitated by adding a concentrated solution of hydrochloric acid to a cold aqueous solution of ββ′-dibromodiethyl selenide dibromide, but it has to be separated from some unchanged dibromide which is precipitated with it. As was expected, the melting point of the

product so obtained was somewhat low (96°), but, on reduction, it gave ββ′-dibromodiethyl selenide identical with an authentic specimen.

Addendum.

The reaction between propylene and selenium tetrachloride has also been carried out. ββ′-Dichlorodipropyl selenide dichloride, m. p. 76·5° (Boord and Cope, *loc. cit.*, give 81°), was obtained in almost theoretical yield. It is conveniently purified by dissolving in cold water, in which it is readily soluble, and reprecipitating with hydrochloric acid (Found: Cl, 46·7; calc., Cl, 46·5%). When reduced with potassium metabisulphite under the usual conditions, it was converted into ββ′-dichlorodipropyl selenide, which has not yet been obtained crystalline (Found: Cl, 30·1; calc., Cl, 30·3%).

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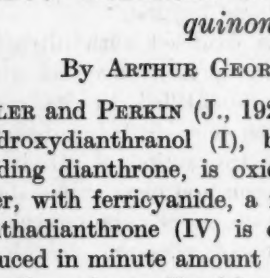
CCLIV.—*Reduction Products of the Hydroxyanthraquinones. Part VI.*

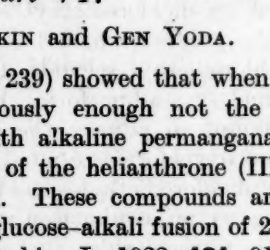
By ARTHUR GEORGE PERKIN and GEN YODA.

HALLER and PERKIN (J., 1924, **125**, 239) showed that when 3 : 6′-dihydroxydianthranol (I), but curiously enough not the corresponding dianthrone, is oxidised with alkaline permanganate or, better, with ferricyanide, a mixture of the helianthrone (III) and naphthadianthrone (IV) is obtained. These compounds are also produced in minute amount by the glucose–alkali fusion of 2-hydroxyanthraquinone (Bradshaw and Perkin, J., 1922, **121**, 913).

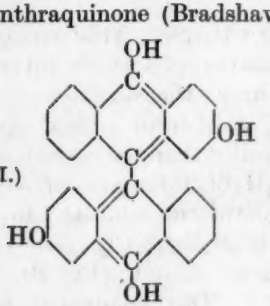
(I.)



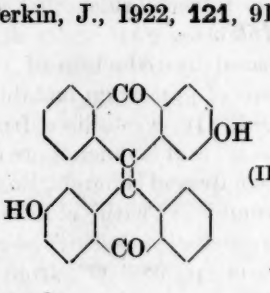
(II.)



(III.)



(IV.)



It appeared likely that the first product of the oxidation would be the dihydroxydianthraquinone (II) and it was actually found by Perkin and Haller (*loc. cit.*) that by the more gentle action of ferricyanide a product was obtained which seemed to consist of this substance in an impure condition. Experiment has now shown that this dihydroxydianthraquinone can be prepared in good yield by the action of iodine on a pyridine solution of tetra-acetyldihydroxydianthranol at about 80°, diacetoxydianthrone remaining unchanged under these conditions. This substance, apparently the first hydroxydianthraquinone to be prepared, consists of pale yellow leaflets, blackens about 280°, and does not appear to have a definite melting point. Though two formulæ are applicable to this compound, in which hydroxyls occupy either the 3 : 6′-* or 3 : 3′-positions, it evidently consists in the main of a single substance, because on oxidation with alkaline ferricyanide an excellent yield of the dihydroxyhelianthrone (III) is produced. On the other hand, whereas the melting point of the diacetyldianthraquinone, after crystallisation from acetic anhydride, is 293—295°, and this can be raised by repeated fractionation from tetrachloroethane to about 314—316° without apparent alteration in the character of the substance, it is possible that a small amount of a second variety is also produced. The melting points given of the dibenzoyl compound, 301—302°, and the dimethyl ether, 290—292°, vary to some extent with the rapidity of heating, but on the whole there is no definite evidence that the new dihydroxydianthraquinone consists of two isomerides. 3 : 3′-Dihydroxydianthraquinone (m. p. 293—295°) is easily reduced by zinc dust and ammonia to 3-hydroxyanthranol, but is unaffected by long treatment with sulphur dioxide in the presence of alcohol. By digestion with 3-hydroxyanthranol in boiling acetic acid solution 3 : 3′-dihydroxydianthrone is slowly produced, whereas acetyldihydroxydianthraquinone with chromic acid in the same solvent gives 2-acetoxyanthraquinone. Dihydroxydianthraquinone is more quickly affected by light than the corresponding helianthrone (*loc. cit.*), the pale yellow crystals rapidly becoming orange-coloured, evidently with production first of the latter compound; this change even occurs to some extent during crystallisation from much boiling acetone. Though the diacetyl and dimethyl compounds are less sensitive in the solid condition to light than the corresponding dihydroxy-derivative, after 5 weeks' exposure to light their

* Experiments in progress render it uncertain as to whether the dihydroxydianthranol reacts in these cases as the 3 : 6′-compound as was suggested (*loc. cit.*), but as the work is incomplete such formulæ are still employed for the present.

solutions in benzene had deposited diacetoxynaphthadianthrone and dimethoxynaphthadianthrone containing a little dimethoxyhelianthrone, respectively. It is thus evident that in these circumstances the helianthrone formation precedes that of the naphthadianthrone.

EXPERIMENTAL.

Tetra-acetyldihydroxydianthranol (0·5 g.) dissolved in pyridine (5 c.c.) was treated with a solution of iodine (0·5 g.) in pyridine (5 c.c.) and kept at 80° for 1½ hours. The reddish-brown liquid was poured into a freshly-acidified solution of sodium bisulphite, and the greenish-yellow precipitate collected and dried. On digestion with boiling acetic anhydride and pyridine for about ½ minute, crystals separated and when cold these were collected and recrystallised from much acetic anhydride. The acetyl compound thus produced became greenish-black at about 280°, melted at 293—295° (A), and was unaltered by further recrystallisation from the same solvent. On the other hand, by repeated crystallisation from tetrachloroethane or a mixture of this with acetic anhydride, the melting point rose to 314—316° (B) [Found: (A) C, 76·7; H, 4·2. (B) C, 76·6; H, 4·0; $CH_3 \cdot CO_2H$, 23·9. $C_{32}H_{20}O_6$ requires C, 76·8; H, 4·0; $CH_3 \cdot CO_2H$, 24·0%].

Owing to its sparing solubility in alcohol, the substance for the acetyl determination was dissolved in cold sulphuric acid overnight; the solution was then diluted with alcohol and treated in the usual manner. 3 : 6′-*Diacetoxydianthraquinone* forms small, pale yellow crystals sparingly soluble in the usual solvents, the solutions when hot possessing a green colour which fades on cooling; this property, also possessed by 3 : 6′-dihydroxydianthraquinone, appears to be characteristic of dianthraquinone derivatives. When diacetoxydianthraquinone (0·5 g.) in benzene (200 c.c.) was exposed to light for 5 weeks, it yielded an orange-brown, crystalline deposit (0·37 g.). This, on recrystallisation from nitrobenzene with the aid of animal charcoal, yielded pale yellow needles, melting above 350° and soluble in sulphuric acid with a red coloration, consisting evidently of diacetoxynaphthadianthrone (Found: C, 77·2; H, 3·4. $C_{32}H_{16}O_6$ requires C, 77·4; H, 3·3%).

As diacetoxydianthraquinone could not be satisfactorily hydrolysed with mineral acids, its suspension (1 g.) in boiling alcohol (25 c.c.) was treated with 10% caustic soda solution until all had dissolved. The solution was diluted with boiling water (25 c.c.) and immediately neutralised with hydrochloric acid; * pale yellow leaflets

* This operation must be carried out rapidly, otherwise discoloration is liable to occur.

then commenced to separate. After dilution with hot water (25 c.c.) and cooling, the crystals (yield 96% of theoretical) were collected and washed with a little acetone, which removed a trace of a red impurity (Found: C, 80·8; H, 4·0. $C_{28}H_{16}O_4$ requires C, 80·8; H, 3·8%).

Dihydroxydianthraquinone crystallises from pyridine and water in pale yellow plates which become black at about 280° and scarcely have a definite melting point. It is sparingly soluble in the usual solvents, but dissolves in alkalis with an orange-yellow colour which is fairly permanent in air. With sulphuric acid it gives a maroon-coloured liquid quickly passing to brownish-black and from this, after keeping, water precipitates a brown-black precipitate soluble in alkali with a similar colour. This is reduced by sodium hyposulphite to an orange-yellow liquid which quickly oxidises in air. The boiling ammoniacal solution is quickly decolorised by zinc dust, and on acidification deposits crystals, which give an acetyl compound, m. p. 158—159°, identical with 3-acetoxyanthranol. A solution of dihydroxyanthraquinone (0·2 g.) in absolute alcohol (160 c.c.) rapidly became orange-coloured in sunlight and after 6 weeks' exposure had deposited 0·1675 g. of crystals. These, after acetylation and fractional crystallisation of the product, gave 0·1 g. of diacetoxynaphthadianthrone, m. p. above 350°, and a little diacetoxyhelianthrone, m. p. 275—279°.

Dihydroxydianthraquinone is best kept in the dark, as the crystals become orange-coloured in a few hours, owing evidently to the action of light. Dihydroxydianthraquinone (1 g.) in water (25 c.c.) was dissolved by addition of 10% sodium hydroxide solution (3 c.c.), and 20% potassium ferricyanide (9 c.c.) slowly added in the cold. After 15 minutes, the mixture was acidified and the red precipitate collected (1·03 g.). This, after acetylation and recrystallisation of the product from benzene, gave 0·97 g. of diacetoxyhelianthrone, m. p. 277—279° (Found: C, 76·75; H, 3·6. Calc., C, 77·1; H, 3·6%).

Dibenzoyldihydroxydianthraquinone was obtained by heating dihydroxydianthraquinone (0·5 g.), benzoic anhydride (5 g.), and a trace of pyridine at 210° for 2 hours. Addition of alcohol to the partly cooled liquid caused the deposition of crystals, which were washed with an alcoholic solution of benzoic anhydride and finally with alcohol. The product was dissolved in much boiling benzene, the solution filtered and evaporated, when small, yellow plates separated, which darkened at 295° and melted at 301—302° to a green liquid (Found: C, 80·4; H, 3·8. $C_{44}H_{24}O_6$ requires C, 80·7; H, 3·8%).

Dimethoxydianthraquinone was prepared by treating the dihydr-

oxy-compound (1 g.) in methyl alcohol (30 c.c.) with equivalent amounts of methyl sulphate and methyl-alcoholic potash, until no colour change occurred on the addition of the latter. After dilution with hot water the crystals (0·85 g.) were collected, washed with cold alcohol, and dissolved in pyridine; the green solution was treated with a little sodium hydroxide, and hot water cautiously added. The crystals were collected and the latter operation, which has for its object the removal of a trace of incompletely methylated substance, was repeated. By recrystallisation from pyridine, the *dimethoxy*-derivative was obtained in small, rectangular, yellow plates which became green at about 270° and melted at 297—299°. On exposure to light it soon develops an orange colour (Found: C, 81·4; H, 4·5; CH_3, 6·7. $C_{30}H_{20}O_4$ requires C, 81·1; H, 4·5; CH_3, 6·75%).

When dimethoxydianthraquinone (1 g.) is dissolved in the necessary amount of boiling acetone in daylight (1300 c.c. approx.), and the solution evaporated to a small bulk, alteration occurs even during this short period and the crystalline deposit can be separated by fractionation from pyridine into (*a*) dimethoxydianthraquinone, m. p. 297—299°, and (*b*) a very sparingly soluble, orange compound (A), which did not melt at 320° dissolves in sulphuric acid with a red coloration and is probably dimethoxynaphthadianthrone. Again, a solution of dimethoxydianthraquinone (0·3 g.) in benzene (100 c.c.) on exposure to light became orange-coloured in about 30 minutes, and commenced to deposit an orange powder. This (0·128 g.), by crystallisation from nitrobenzene, was obtained in microscopic needles, which had not melted at 340° and were soluble in sulphuric acid with a red coloration. An analysis of the small amount of this compound available was unsatisfactory, but there can be little doubt that this and the compound A referred to above, which closely resembled it, consist of *dimethoxynaphthadianthrone*. The benzene filtrate on evaporation to dryness gave a dark-coloured residue which after solution in hot alcohol yielded yellow crystals; these, after purification, were soluble in sulphuric acid with a violet coloration and had the properties of dimethoxyhelianthrone.

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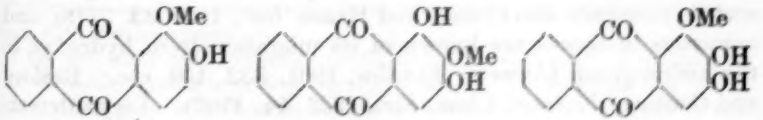
THE UNIVERSITY, LEEDS. [*Received, June 17th*, 1925.]

CCLV.—*A Wandering of the Acetyl Group during Methylation.*

By Onro Kubota and Arthur George Perkin.

Oesch and Perkin (P., 1914, **30**, 213) submitted monoacetylalizarin (J., 1899, **75**, 433) to the action of diazomethane and after hydrolysis isolated from the product a small amount of alizarin 1-methyl ether (1) identical with that obtained from Chay root (J., 1893, **64**, 1160; 1907, **91**, 2068). Reinvestigation has now shown that, although the 1-methyl ether is always produced in this way, the main product is the 2-methyl ether. Careful examination of the monoacetylalizarin employed in these experiments indicated it to be a single substance, and indeed were this not the case it would be more likely to consist of a mixture of mono- and di-acetylalizarins than of the 1- and 2-acetyl derivatives.* The formation of alizarin 2-methyl ether in these experiments shows that whereas a small portion of the 2-acetylalizarin reacts normally with diazomethane, the acetyl group must wander from the 2- to the 1-position at some stage of the process, and the methyl then enters its place to give 2-methoxy-1-acetoxyanthraquinone; the yield of this is about 80% of the theoretical.

2 : 3-Diacetylanthragallol again, which can be readily obtained by the partial acetylation of anthragallol, on treatment with diazomethane gives as the main product a diacetylanthragallol monomethyl ether which evidently contains the methoxy-group in the 2-position, because the free substance (II), which crystallises in yellow needles, is soluble in dilute alkali with a red coloration similar to that given by purpuroxanthin. The more soluble fraction of the reaction product when hydrolysed gave a mixture from which, by means of the sparing solubility of its ammonium salt, the isomeric ether was isolated. This crystallises in orange-red needles, dissolves in alkali with a deep blue colour, and dyes mordanted calico shades of the alizarin type. It must therefore contain adjacent hydroxyls and is clearly anthragallol 1-methyl ether (III) (1-methoxyhystazarin), for if it were anthragallol



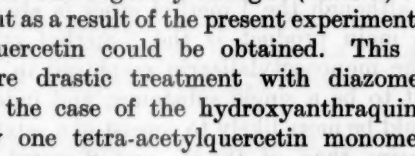
(I.) (II.) (III.)

* It is well known that in the anthraquinone series the 2-hydroxyl group is more readily acetylated than the 1-hydroxyl group (compare Dimroth, Friedemann, and Kämmerer, *Ber.*, 1920, **53**, 481).

3-methyl ether (3-methoxyalizarin) its formation would necessitate the respective wandering of the 2- and 3-acetyl groups into the 1- and 2-positions, or of the 3-acetyl group into the 1-position. It is unfortunate that a monoacetylanthragallol has not yet been obtained, for the action of diazomethane thereon should yield one or other of the anthragallol dimethyl ethers referred to above.

In a third series of experiments, tetra-acetylquercetin was employed, a substance which has been prepared by the action of acetic anhydride and sodium acetate on quercetin in the cold. This substance was originally thought (*loc. cit.*) to be the triacetyl derivative, but as a result of the present experiments only 3 : 7 : 3′ : 4′-tetra-acetylquercetin could be obtained. This acetyl derivative required more drastic treatment with diazomethane than was necessary in the case of the hydroxyanthraquinones, and in the product only one tetra-acetylquercetin monomethyl ether could be detected. The almost colourless, sparingly soluble quercetin monomethyl ether obtained by hydrolysis closely resembled, but is not identical with, the quercetin monomethyl ether, rhamnetin, previously studied (J., 1902, **81**, 469). By decomposition with alcoholic potash, it yielded phloroglucinol monomethyl ether, identified as its benzeneazo-compound, and there can be no doubt that this new quercetin methyl ether contains the methoxy-group in the 5-position adjacent to the carbonyl group (IV).

(IV.)

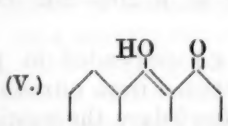


A wandering of the acetyl group does not occur in these circumstances. Interesting is the fact that this 5-methyl ether yields with alcoholic potassium acetate the salt $C_{16}H_{11}O_7K$, for, as quercetin gives a similar compound, it seems clear that the reactive hydroxyl, the position of which has not yet been determined with certainty, cannot be that situated in the 5-position. The wandering of an acetyl group has been observed by Wislicenus and Körner (*Ber.*, 1901, **84**, 218) in the case of the *o*-acetyl derivative of ethyl acetoacetate (compare also Claisen and Haase, *Ber.*, 1900, **33**, 3778), and numerous instances are known of its migration from hydroxyl to the amino-group (Auwers, *Annalen*, 1901, **332**, 159, etc.; Raiford and Couture, *J. Amer. Chem. Soc.*, 1922, **44**, 1792). Very interesting, again, is the work of Fischer, Bergmann, and Lipschitz (*Ber.*, 1918, **51**, 45), who showed that 3 : 4 : 5 : 3′ : 5′-penta-acetyl(para)-digallic acid, when hydrolysed, yields the 3 : 4 : 5 : 3′ : 4′-penta-hydroxy-*m*-digallic acid, a wandering of the galloyl nucleus from

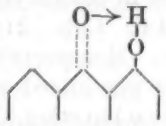
the *p*- to the *m*-position occurring. Again, 3 : 5-diacetyl-4-benzoylgallic acid on hydrolysis in a similar manner yields not the *p*- but the *m*-benzoyl derivative, and a similar change has been observed in the case of 3-acetyl-4-benzoylprotocatechuic acid. Herzig and Tichatschek (*Ber.*, 1908, **39**, 268, 1557) have shown that under the influence of diazomethane the acetyl group in triacetylpyrogallol is partly replaced by methyl, whereas acetylphloroglucinol diethyl ether gives phloroglucinol methyl diethyl ether * in the same circumstances.

p-Acetoxybenzoic and *m*-hydroxybenzoic acids are mainly converted by diazomethane into the corresponding methoxybenzoic acids. The results of this investigation, however, differ † from the cases just mentioned in that the wandering of the acetyl group occurs during methylation itself, and though it was scarcely necessary to do so, this has been proved by an examination of the reaction products of each experiment. It is well known in the case of substances such, for instance, as β-resorcylic acid (J., 1895, **67**, 990), luteolin (J., 1900, **77**, 1316), and quercetin (J., 1913, **103**, 1632), all of which contain meta-hydroxyl, that on methylation with methyl iodide the methyl group in part, rather than substitute the hydrogen of the hydroxyl next to the carbonyl group, actually enters the ring. In the cases of 2-acetylalizarin and of 2 : 3-diacetylanthragallol, this cannot occur, and with 3 : 7 : 5′ : 4′-tetra-acetylquercetin this would appear to be prevented by the presence of the 3-acetyl group.

This curious interchange of methyl and acetyl is without doubt connected with the peculiar property of the hydroxyl adjacent to the carbonyl group,‡ and it has been suggested that this may be due to the existence of the ortho-quinonoid arrangement (V) (*loc. cit.*). Dimroth and Faust (*Ber.*, 1921, **54**, 3020) presume that there is an unstable valency between the ketonic oxygen and the



(V.)



(VI.)

* Experiment has shown that diacetylalizarin is not affected by treatment with diazomethane.

† On the other hand, when 2-acetylalizarin 1-methyl ether is hydrolysed with alcoholic ammonia or with hydrochloric acid the resulting free ether, which when pure is yellow, is always contaminated with a trace of red impurity which may be removed with baryta water. Although a wandering of the methyl group with formation of alizarin 2-methyl ether may be suspected, this is as yet uncertain.

‡ Or, as the result of the work of Fischer (*loc. cit.*), of that in the para-position thereto.

hydrogen of the 1-hydroxyl group, a view also taken by Sidgwick and Callow (J., 1924, **125**, 527), who suppose that a six-membered chelate ring (VI) exists in compounds of this type.

A grouping of this kind evidently does not exist, or is much weakened, when an acyl or an alkyl group is substituted for the hydrogen of the 1-hydroxyl group, since such substances possess the pale yellow colour characteristic of anthraquinone itself, and if this chelate ring is present, the ease or otherwise with which this substitution takes place will depend upon the readiness with which this linking is broken or weakened. It is very difficult to compare the relative facility with which the processes of acetylation and methylation occur, but acetylation of the hydroxyl in the 1-position in the presence of a catalyst takes place so readily that it may be assumed to occur with more facility than the process of methylation. Even if this is so, it is difficult to understand why the acetyl group, which, similarly to the methyl group, favours the 2-position, should wander to the 1-position in the circumstances mentioned above, unless indeed 1-acetylalizarin 2-methyl ether is a more stable substance than 2-acetylalizarin 1-methyl ether.* Experiments to determine whether a conversion of the latter into the former can be effected are in progress, and the behaviour of other acyl groups in similar circumstances is also being studied.

Experimental.

Monoacetylalizarin.—A mixture of commercial alizarin (5 g.), potassium acetate (2·5 g.), and acetic anhydride (25 c.c.) is kept for 24 hours, and then diluted with alcohol. The product, collected after 1 hour and recrystallised repeatedly from alcohol–acetic acid, separates in golden-yellow needles, m. p. 204—206° (Found: $CH_3 \cdot CO_2H$, 21·0. Calc., 21·3%).

Methylation. Monoacetylalizarin (2 g.) suspended in purified ether (50 c.c.) was mixed with diazomethane from nitrosomethylurethrane (12 c.c.) in ether (200 c.c.). After 5 days, the crystals were collected (1·8 g.) and the mother-liquor was evaporated to dryness; the viscid residue, on digestion with methyl alcohol, deposited a further 0·16 g. of acetylalizarin monomethyl ether (Found: $CH_3 \cdot CO_2H$, 20·3. $C_{17}H_{12}O_5$ requires $CH_3 \cdot CO_2H$, 20·2%). After hydrolysis with hydrochloric acid in the presence of acetic acid, the product, which sintered at 170° and melted at 217°, gave, after two or three recrystallisations from alcohol, orange-red needles,

* That the methyl of alizarin 1-methyl ether is loosely held, is evident from the fact that in presence of boiling baryta water, gradual hydrolysis occurs, with formation of barium alizarate.

m. p. 229—230° (Found: C, 70·8; H, 4·05. $C_{15}H_{10}O_4$ requires C, 70·9; H, 3·9%).

The *acetyl* derivative, obtained in yellow needles, melted at 204—206° and there could be no doubt that this, the main product of the reaction, is alizarin 2-monomethyl ether.

The alcoholic filtrate from this substance was evaporated to dryness, the residue dissolved in hot alcohol, and, after the addition of a little ammonia, baryta water was added drop by drop so long as a precipitate, consisting mainly of barium alizarate 2-methyl ether, was formed. This was removed, and on acidifying the bright red filtrate fine, hair-like needles (0·18 g.) separated.* This substance, which became opaque at 100° with loss of water of crystallisation, a characteristic property of alizarin 1-methyl ether, was purified by conversion into the ammonium salt (*loc. cit.*) and recrystallisation from benzene, from which it separated in pale yellow needles, m. p. 179—181° (Found: C, 70·9; H, 4·0. Calc., C, 70·9; H, 3·9%).

Since the acetyl derivative melted at 210—212°, there can be no doubt that this substance was identical with the alizarin 1-methyl ether of Chay root. By fractionally crystallising the diazomethane reaction product of 2-acetylalizarin (2 g.) from a mixture of alcohol and acetic acid, 2-acetylalizarin 1-methyl ether could be isolated in the pure condition (0·3 g. approx.).

Diacetylanthragallol.—A mixture of anthragallol (5 g.), acetic acid (15 c.c.), and acetic anhydride (7 c.c.) was treated in the cold with pyridine (2 c.c.) and kept for about 18 hours. The yellow, crystalline precipitate (5·79 g.) (filtrate A) gave on recrystallisation from acetone 4·3 g. of long, thin plates, m. p. 223—224° (Found: $C_{14}H_8O_5$, 74·4. $C_{18}H_{12}O_7$ requires $C_{14}H_8O_5$, 75·3%).

The filtrate A contained some triacetylanthragallol, which was isolated in a slightly impure condition, m. p. 175—180° (Found: $C_{14}H_8O_5$, 66·9. $C_{20}H_{14}O_8$ requires $C_{14}H_8O_5$, 67·02%).

Methylation. Diacetylanthragallol (2 g.), in ether (50 c.c.) cooled by ice, was treated with diazomethane from nitrosomethylurethrane (8 c.c.) in ether (250 c.c.), and the mixture kept for 2 days. The crystalline suspension (1 g.), after being washed with ether, melted at 145—152°. The filtrate, washed with a little 1% sodium hydroxide solution and partially evaporated, gave 0·75 g. of crystals (filtrate A). By recrystallisation from acetone, large, yellow, prismatic needles were obtained, m. p. 152—154° (Found: C, 64·55; H, 4·15; CH_3, 4·3. $C_{19}H_{14}O_7$ requires C, 64·4; H, 3·95; CH_3, 4·23%).

Hydrolysis with hydrochloric acid in acetic acid solution gave

* In a second experiment 4 g. of monoacetylalizarin gave 0·32 g. of alizarin 1-methyl ether.

78·5% of a yellow, crystalline precipitate which separated from much benzene as a spongy mass of microscopic needles, m. p. 218—220° (Found: C, 66·9; H, 3·7; CH_3, 5·55%).

This substance dissolves in dilute alkali with a scarlet colour and is evidently *anthragallol 2-monomethyl ether*, since the alkali solutions of anthragallol 1- and 3-methyl ethers have a blue or bluish-violet tint. The filtrate A was evaporated to dryness and the residue dissolved in hot alcohol mixed with a few drops of ammonia. On keeping, violet-black crystals of an ammonium salt separated which, on drying at 100°, evolved ammonia, yielding an orange-red mass. By recrystallisation from alcohol, this gave red needles (0·3 g.), m. p. 239—241° (Found: C, 66·6; H, 3·9; CH_3, 5·6. $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7; CH_3, 5·55%).

It dissolves in dilute alkalis with a deep blue colour and dyes mordanted wool the following alizarin-like shades: *chromium*, violet-maroon; *aluminium*, pale maroon; *tin*, orange-red; *iron*, dead black. The diacetyl derivative, obtained as fine, flat, yellow needles, melted at 203—205° (Found: C, 64·5; H, 4·2. $C_{19}H_{15}O_7$ requires C, 64·4; H, 3·95%).

For reasons given in the introduction, this compound is evidently *anthragallol 1-methyl ether*.

Tetra-acetylquercetin.—A mixture of monopotassium quercetin (10 g.) and acetic anhydride (100 g.) was kept for 2 hours. The semi-solid mass was mixed with alcohol; the crystals were then collected and recrystallised from alcohol–acetic acid until the melting point of the colourless, silky needles was constant at 188—190° (Found: $C_{15}H_{10}O_7$, 64·4. $C_{23}H_{18}O_{11}$ requires $C_{15}H_{10}O_7$, 64·25%).

Methylation. Tetra-acetylquercetin suspended in ether was very little attacked by diazomethane and after keeping for 2 days contained only 1·08% of methyl. Better results were obtained by treating the substance (2 g.), dissolved in tetrachloroethane (10 c.c.), with the diazomethane from nitrosomethylurethane (8 c.c.) in ether (125 c.c.). After 4 days, the crystalline deposit (1·7 g.) was collected, and from the filtrate, by removal of the ether by evaporation and the tetrachloroethane by distilling with steam, a colourless, viscid product was isolated from which, by solution in hot alcohol and keeping, a second crop of crystals was obtained. The product was hydrolysed with hydrochloric acid in the usual manner and the precipitate, which consisted largely of an oxonium salt, was repeatedly washed with water to decompose the latter. The product was then dissolved in much alcohol, the solution concentrated until crystallisation commenced, and the operation repeated. The *quercetin monomethyl ether* separated in prismatic

needles, m. p. 305—308° (Found: C, 60·65; H, 4·2; CH_3, 4·2. $C_{16}H_{12}O_7$ requires C, 60·75; H, 3·8; CH_3, 4·6%).

This methyl ether closely resembles rhamnetin (*loc. cit.*) as regards its sparing solubility in solvents, but, on the other hand, it is almost colourless, whereas rhamnetin is yellow. Dilute alkalis dissolve it with an orange coloration and on hydrolysing its acetyl derivative with mineral acids, orange-red oxonium salts can be obtained which crystallise in needles.

The *tetra-acetyl* derivative crystallises from acetone in minute, colourless needles which sinter at 199° and melt at 202—204° (Found: C, 59·5; H, 4·2. $C_{24}H_{20}O_{11}$ requires C, 59·5; H, 4·1%).

Only by very slow deposition from a mixture of acetic anhydride and alcohol can the acetyl derivative be obtained in fair-sized, prismatic needles, whereas acetylrhamnetin crystallises readily in long needles, m. p. 191—193°. When the acetyl compound was digested with boiling alcoholic potassium acetate, lemon-yellow needles of the *monopotassium* salt were gradually deposited, and these were washed with alcohol (Found: K, 11·1. $C_{16}H_{11}O_7K$ requires K, 11·0%).

This potassium salt dissolves in boiling water to form a pale yellow solution, from which on rapid cooling it separates unchanged. On longer digestion, however, some hydrolysis occurs with deposition of the quercetin methyl ether, though it is more resistant to hydrolysis than monopotassium quercetin itself.

The hydrolysis of the quercetin monomethyl ether was effected by heating with methyl-alcoholic potash at 180° for 3 hours. The product freed from alcohol was dissolved in water, and the solution acidified, filtered, and extracted with ether; the syrupy residue obtained by evaporation was then dissolved in sodium bicarbonate solution, and again extracted with ether. The viscid product thus isolated gave with diazobenzene in presence of sodium carbonate a dull red precipitate, which was dried, extracted with boiling alcohol to remove resin, and then crystallised from alcohol–acetic acid. The glistening, orange-red crystals, m. p. 253—255°,* evidently consisted of benzeneazophloroglucinol monomethyl ether. In a second experiment air was aspirated through a dilute alkaline solution of the quercetin methyl ether and, from the brown liquid, phloroglucinol monomethyl ether could again be isolated in the form of its benzene azo-compound.

For reasons given in the introduction, this quercetin monomethyl ether must contain the methoxy-group in the position 5, adjacent to the carbonyl group (IV). The methylation of this hydroxyl

* The m. p. 250—252° previously given for this compound (*loc. cit.*) is slightly too low.

group has no influence on the tinctorial property of quercetin, as dyeing experiments employing mordanted woollen cloth show: *chromium*, red-brown; *aluminium*, orange-yellow; *tin*, bright orange; *iron*, olive-black.

These shades were identical with those given by a sample of quercetin dyed at the same time (J., 1902, **81**, 473) and as quercetin and rhamnetin dye alike (Perkin and Allison) there can be no doubt that the phloroglucinol hydroxyl groups of quercetin do not affect its tinctorial property.

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CCLVI.—*Hydrogen and Oxygen Electrode Titrations of Some Dibasic Acids and of Dextrose.*

By HUBERT THOMAS STANLEY BRITTON.

APART from the recent work of Auerbach and Smolczyk (*Z. physikal. Chem.*, 1924, **110**, 83), the study of the ionisation of dibasic acids has been confined to solutions containing (*a*) the free acids and (*b*) the acid salts only, instead of to solutions which are typical of the whole courses of neutralisation. Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 847) obtained several titration curves with the hydrogen electrode, but as he used fairly concentrated solutions and appears to have aimed at an accuracy in his *E.M.F.* measurements of about a centivolt, his curves are useless for the purpose of calculating dissociation constants.

Auerbach and Smolczyk used the quinhydrone electrode in their titrations and derived formulæ by which the dissociation constants could be calculated from their data. Although their equations are based on the assumption that the salts formed in dilute solutions may be taken as being completely dissociated, they used $N/10$-acid and $N/8$-alkali solutions. The amounts of alkali used in their titrations were very small, being as a rule only 8 c.c. It is remarkable that such fundamental titrations should have been carried out with an electrode other than the hydrogen electrode. Some time before the appearance of Auerbach and Smolczyk's paper, the author had used the hydrogen electrode to titrate solutions of acids which were more dilute and required much larger volumes of alkali. Those titrations had been made for the purpose of comparing them with those given by oxygen electrodes; as the accuracy of the voltages obtained with the hydrogen electrode was of the order of a millivolt, it was considered that the curves would furnish an excellent

method of testing the applicability of the formulæ of Auerbach and Smolczyk.

The titration of dextrose has been included in this communication as it is of importance in connexion with some work to be published later.

Experimental.

Part I. *The Hydrogen Electrode.*

The problem of preparing hydrogen electrodes which are immediately sensitive to changes in hydrogen-ion concentration has been one of some difficulty, and this appears to have been the experience of previous experimenters. Thus Böttger (*Z. physikal. Chem.*, 1897, **24**, 251), who first used the hydrogen electrode for titration work, failed to obtain good results with platinised platinum and resorted to gold electrodes coated with palladium black. Andrews (*J. Biol. Chem.*, 1924, **50**, 479) has, however, found palladium black on platinum to be less trustworthy than platinum black. Treadwell and Weiss (*Helv. Chim. Acta*, 1920, **2**, 433) stated that the ordinary platinum electrode required too much time to come to equilibrium to be of use in titrations, and they also preferred palladinised gold.

For ordinary purposes, there is no doubt that the hydrogen electrode when made of platinised platinum does attain, if given sufficient time, true equilibrium, independent of the depth of the platinum black layer. Platinum foil electrodes having a thick coating of platinum black require, in general, an appreciable time before the true *E.M.F.*'s are attained, and are therefore unserviceable for titrations. The efficient electrodes which have been prepared have invariably been made of highly polished platinum foil covered with thin deposits of platinum black such as may be deposited from the usual platinising solution in 5 minutes, the current being reversed every half-minute and a vigorous evolution of gas maintained. Half a dozen electrodes were prepared at a time from which were chosen two electrodes which gave the same *E.M.F.* within a millivolt throughout the entire titration. These two electrodes were used together and the results were taken as accurate if they showed the same *E.M.F.* immediately the current of hydrogen was stopped. Other efficient electrodes were always kept in readiness in case one suddenly became erratic or sluggish, which was especially apt to occur when the electrode was being subjected to a rapid change in hydrion concentration.

The electrodes were of the Hildebrand pattern (*loc. cit.*) and the titrations were performed in the way described previously (J., 1924, **125**, 1576). The results obtained are given in the first two

columns of Tables I—V, the *P.D.*'s being recorded to the nearest millivolt.

TABLE I.

Titration of 100 c.c. of 0·0255*M*-Oxalic Acid with 0·100*N*-NaOH at 18°.

C.c. of NaOH.	*E.M.F.* against *N*-calomel. —Volt.	p_H.	Conc. of free $H_2C_2O_4$ $\times 10^2$.	a.	$[H_2C_2O_4]$ (undissociated) $\times 10^3$.	$[HC_2O_4']$ $\times 10^2$.	K_1.
0	0·378	1·65	2·55	0·89	2·90	2·26	0·19
2·5	0·382	1·72	2·15	0·90	2·15	2·18	0·19
5·0	0·385	1·75	1·99	0·88	2·49	2·23	0·17
7·5	0·389	1·84	1·67	0·87	2·14	2·15	0·15
10·0	0·393	1·91	1·41	0·88	1·69	2·15	0·16
12·5	0·397	1·98	1·16	0·92	0·92	2·17	0·25
15·0	0·403	2·08	0·91	0·91	0·82	2·13	0·22
17·6	0·409	2·18	0·67	0·98	0·13	2·15	1·32
20·0	0·418	2·34	0·46	1·00	—	—	—
22·0	0·429	2·53	0·29	1·03	—	—	—
23·5	0·437	2·67	0·16	1·32	—	—	—
24·5	0·444	2·79	0·08	2·02	—	—	—
25·1	0·446	2·83	0·03	4·68	—	—	—

			$Na_2C_2O_4$.	$NaHC_2O_4$.	$K_2 \times 10^4$.
26·0	0·453	2·95	0·5	25·0	0·23
27·0	0·457	3·02	1·5	24·0	0·60
28·0	0·460	3·07	2·5	23·0	0·93
30·0	0·474	3·31	4·5	21·0	1·05
32·5	0·484	3·48	7·0	18·5	1·25
35·0	0·493	3·64	9·5	16·0	1·36
37·5	0·502	3·80	12·0	13·5	1·43
40·0	0·511	3·95	14·5	11·0	1·48
42·5	0·524	4·18	17·0	8·5	1·33
45·0	0·537	4·40	19·5	6·0	1·29
47·0	0·547	4·58	21·5	4·0	1·43
49·0	0·568	4·94	23·5	2·0	1·35
50·0	0·593	5·37	24·5	1·0	1·04
50·5	0·622	5·88	25·0	0·5	0·67
51·0	0·745	8·00			
52·0	0·894	10·59			
52·5	0·913	10·91			
55·0	0·942	11·42			
57·0	0·956	11·66			
60·0	0·970	11·91			

The third column of each table gives the p_H calculated by means of the Nernst formula. The figures in the remaining columns of the first four tables were obtained on the assumption that the alkali (up to the first equivalent) reacted only with the hydrions arising from the first stage of ionisation and that thereafter it reacted (to the second equivalent) with those from the second dissociation. This assumption, of course, is only justifiable when K_1 is much greater than K_2, but the figures so obtained do give some idea of the process of neutralisation in the cases where the ratio of K_1 to K_2 is small. The fourth columns relating to the first halves

TABLE II.

Titration of 100 c.c. of 0·0250*M*-Tartaric Acid with 0·100 *N*-NaOH at 18°.

C.c. of NaOH.	*E.M.F.* against *N*-calomel —Volt.	p_H.	Conc. of free tartaric acid × 10^3.	α.	$[H_2T]$ × 10^3.	$[HT']$ × 10^3.	K_1 × 10^3.
0	0·415	2·29	25·0	0·206	19·9	—	1·34
2·5	0·423	2·43	22·0	0·170	18·3	6·18	1·27
5·0	0·430	2·55	19·0	0·149	16·2	7·60	1·33
7·5	0·437	2·67	16·3	0·132	14·1	9·29	1·41
10·0	0·444	2·79	13·6	0·119	12·0	10·7	1·45
12·5	0·450	2·89	11·1	0·115	9·8	13·4	1·61
15·0	0·457	3·02	8·70	0·111	7·7	14·0	1·75
17·5	0·463	3·12	6·38	0·119	5·6	15·7	2·11
20·0	0·470	3·24	4·17	0·138	3·6	17·2	2·76
21·25	0·473	3·29	3·09	0·164	—	—	—
22·5	0·477	3·36	2·04	0·213	—	—	—
23·75	0·480	3·41	1·01	0·382	—	—	—
25·0	0·4835	3·474	—	—	—	—	—

			Na_2T.	NaHT.	K_2 × 10^5.
27·5	0·490	3·59	2·5	22·5	2·87
30·0	0·496	3·69	5·0	20·0	5·08
32·5	0·506	3·87	7·5	17·5	5·85
35·0	0·514	4·00	10·0	15·0	6·62
37·5	0·523	4·16	12·5	12·5	6·92
40·0	0·529	4·26	15·0	10·0	8·19
42·55	0·540	4·45	17·55	7·45	8·30
45·0	0·551	4·64	20·0	5·0	9·08
46·25	0·559	4·78	21·25	3·75	9·35
47·5	0·571	4·99	22·5	2·5	9·19
48·5	0·587	5·27	23·5	1·5	8·43
49·0	0·604	5·56	24·0	1·0	6·56
49·25	0·616	5·77	24·25	0·75	5·48
49·5	0·637	6·14	24·5	0·5	3·59
49·75	0·664	6·60	24·75	0·25	2·47
50·0	0·822	9·34			
50·5	0·884	10·42			
51·0	0·901	10·71			
52·5	0·928	11·18			
55·0	0·945	11·48			
57·5	0·956	11·66			
60·0	0·961	11·75			

of the titrations therefore contain the concentration of acid minus that which was supposed to be converted into the acid salt. The degree of dissociation, α, of the free acid given in the fifth column, was obtained by dividing the hydrogen-ion concentration by the concentration of the acid. Column 6 gives the concentration of undissociated acid. The concentrations of HR′ ions given in the next column represent the sum of the concentrations of NaHR (taken as completely dissociated into $Na^{\cdot}$ and HR′) and the HR′ ions from the free H_2R. In the last column the values of K_1 ($=[H^{\cdot}][HR']/[H_2R]$ are given.

If the first equivalent of alkali be regarded as producing acid

TABLE III.

Titration of 100 c.c. of 0·0240*M*-Succinic Acid with 0·100*N*-NaOH at 18°.

C.c. of NaOH.	*E.M.F.* against *N*-calomel. —Volt.	p_H.	Conc. of free succinic acid × 10^3.	α.	[H_2Suc.] × 10^3.	[HSuc.′] × 10^3.	K_1 × 10^3
0	0·446	2·83	24·0	0·0623	22·5	—	9·95
2·5	0·467	3·19	21·0	0·0309	20·3	3·09	9·86
5·1	0·482	3·45	18·0	0·0198	17·6	5·21	10·51
7·5	0·495	3·67	15·4	0·0140	15·1	7·35	10·28
10·0	0·508	3·90	12·7	0·0099	12·6	9·22	9·23
12·5	0·518	4·07	10·2	0·0083	10·1	11·20	9·36
15·0	0·524	4·18	7·83	0·0085	7·8	13·1	11·3
17·5	0·532	4·32	5·53	0·0088	5·5	14·9	13·2
20·0	0·540	4·45	3·33	0·0106	3·3	16·7	17·8
22·0	0·547	4·58	1·64	0·0162	1·6	18·1	29·8
23·0	0·550	4·63	0·81	0·0290	7·9	18·7	55·9
24·0	0·556	4·73	—	—	—	—	—

			Na_2Suc.	NaHSuc.	K_2 × 10^6.
25·0	0·557	4·75	1·0	23·0	0·78
27·5	0·564	4·87	3·5	20·5	2·30
30·0	0·570	4·97	6·0	18·0	3·54
32·5	0·579	5·13	8·5	15·5	4·06
35·0	0·588	5·29	11·0	13·0	4·39
37·5	0·596	5·42	13·5	10·5	4·84
40·0	0·608	5·63	16·0	8·0	4·67
42·5	0·621	5·86	18·5	5·5	4·68
44·0	0·630	6·01	20·0	4·0	4·85
45·0	0·639	6·17	21·0	3·0	4·74
46·1	0·654	6·43	22·1	1·9	4·32
47·0	0·670	6·71	23·0	1·0	4·52
47·25	0·681	6·90	23·25	0·75	3·92
47·5	0·694	7·12	23·5	0·5	3·55
47·75	0·733	7·80	23·75	0·25	1·51
48·0	0·807	9·08			
48·5	0·857	9·95			
49·0	0·885	10·43			
50·0	0·920	11·04			
52·5	0·943	11·44			
55·1	0·956	11·66			
57·5	0·963	11·79			
60·0	0·969	11·89			

salt only, the addition of further alkali will convert equivalent amounts into Na_2R. Then $K_2 = [H^\cdot][R'']/[HR']$ may be calculated if the NaHR and Na_2R be taken as either completely or equally dissociated into $Na^\cdot$ and HR', and $2Na^\cdot$ and R'' respectively, in which case $K_2 = [H^\cdot](x - y/2)/(y - x)$, where x is the number of c.c. of NaOH added, and y the number of c.c. required for neutralisation. For the second half of the titrations, the fourth and fifth columns give the number of c.c of alkali, $(y - x)$ and $(x - y/2)$ respectively, which are proportional to the respective concentrations of NaHR and Na_2R. The values of K_2 thus found are given in the last column.

TABLE IV.

Titration of 100 c.c. of 0·0230*M*-Malonic Acid with 0·100*N*-NaOH at 18°.

C.c. of NaOH.	*E.M.F.* against *N*-calomel. —Volt.	p_H.	Conc. of free malonic acid × 10^3.	α.	$[H_2M]$ × 10^3.	$[HM']$ × 10^3.	K_1 × 10^3.
0	0·411	2·28	23·0	0·263	16·9	—	2·16
2·5	0·420	2·37	20·0	0·211	15·8	6·67	1·79
5·0	0·427	2·50	17·1	0·186	14·0	7·95	1·82
7·5	0·433	2·60	14·4	0·175	11·9	9·65	2·04
10·0	0·440	2·72	11·8	0·161	9·91	11·0	2·12
12·5	0·448	2·86	9·34	0·148	7·95	12·5	2·17
15·0	0·458	3·03	6·96	0·133	6·03	14·0	2·15
17·5	0·470	3·24	4·68	0·123	4·11	15·5	2·16
18·5	0·477	3·36	3·80	0·115	3·36	16·0	2·07
20·0	0·487	3·54	2·50	0·117	2·21	17·0	2·24
21·0	0·495	3·67	1·66	0·128	1·45	17·6	2·58
22·0	0·509	3·85	0·82	0·173	0·68	18·2	3·81
22·5	0·515	4·02	0·41	0·233	0·41	18·5	5·62
23·0	0·520	4·11	—	—	—	—	—

			Na_2M.	NaHM.	K_2 × 10^6.
23·5	0·525	4·19	0·5	22·5	1·42
24·0	0·530	4·28	1·0	22·0	2·38
25·0	0·538	4·42	2·0	21·0	3·63
27·5	0·560	4·80	4·5	18·5	3·86
30·1	0·571	4·99	7·1	15·9	4·56
32·5	0·580	5·15	9·5	13·5	5·02
35·0	0·589	5·30	12·0	11·0	5·43
37·5	0·598	5·46	14·5	8·5	5·93
40·0	0·616	5·77	17·0	6·0	4·80
42·0	0·630	6·01	19·0	4·0	4·61
43·0	0·638	6·15	20·0	3·0	4·70
44·0	0·649	6·34	21·0	2·0	4·76
45·0	0·673	6·76	22·0	1·0	3·83
45·25	0·684	6·95	22·25	0·75	3·34
45·5	0·700	7·23	22·5	0·5	2·67
45·75	0·749	8·08	22·75	0·25	0·76
46·0	0·821	9·32			
46·25	0·849	9·81			
46·5	0·869	10·16			
47·0	0·895	10·60			
48·5	0·925	11·13			
50·0	0·940	11·39			
52·5	0·953	11·61			
55·0	0·961	11·75			
57·5	0·966	11·84			
60·0	0·971	11·92			

The titration curves together with that of dextrose are given in Fig. 1. The curve of the latter shows that dextrose had the effect of depressing the alkalinity of the added sodium hydroxide. The monobasic acid nature of dextrose, $C_6H_{12}O_6 \rightleftharpoons H^{\cdot} + C_6H_{11}O_6'$, is revealed in the formation of salts with the alkali metals. The dissociation constant, $K = [H^{\cdot}][C_6H_{11}O_6']/[C_6H_{12}O_6]$, has been calculated from the various observations made during the titration.

TABLE V.

Titration of 140 c.c. of 0·3572*M*-Dextrose with 0·100*N*-NaOH at 18°.

C.c. of NaOH.	*E.M.F.* against *N*-calomel. —Volt.	p_H.	Conc. of NaOH × 10^3.	Total conc. of NaOH and NaGluc. × 10^3.	Conc. of NaGluc. × 10^3.	Conc. of undiss. glucose.	$K = \frac{[H:][Gluc']}{[HGluc.]} \times 10^{13}$.
0	0·645	6·27	—	—	—	0·3572	8·07*
0·5	0·808	9·10	0·009	0·356	0·347	0·3557	7·75*
1·0	0·833	9·53	0·025	0·709	0·684	0·3539	5·70
3·0	0·860	10·00	0·07	2·10	2·03	0·3477	5·84
5·0	0·870	10·35	0·16	3·45	3·29	0·3416	4·30
10·0	0·887	10·47	0·21	6·67	6·46	0·3300	6·63
20·0	0·909	10·85	0·51	12·5	12·0	0·3005	5·65
30·0	0·920	11·04	0·79	17·6	16·8	0·2773	5·53
40·0	0·927	11·16	1·05	22·2	21·1	0·2567	5·69
50·0	0·933	11·27	1·35	26·3	24·9	0·2383	5·61
60·0	0·938	11·35	1·62	30·0	28·4	0·2216	5·72
70·0	0·941	11·40	1·82	33·3	31·5	0·2066	6·07
80·0	0·946	11·49	2·24	36·4	34·2	0·1931	5·73
90·0	0·948	11·53	2·46	39·1	36·6	0·1808	5·97
100·0	0·950	11·55	2·57	41·7	39·1	0·1693	6·51

Mean 5·77 × 10^{-13}

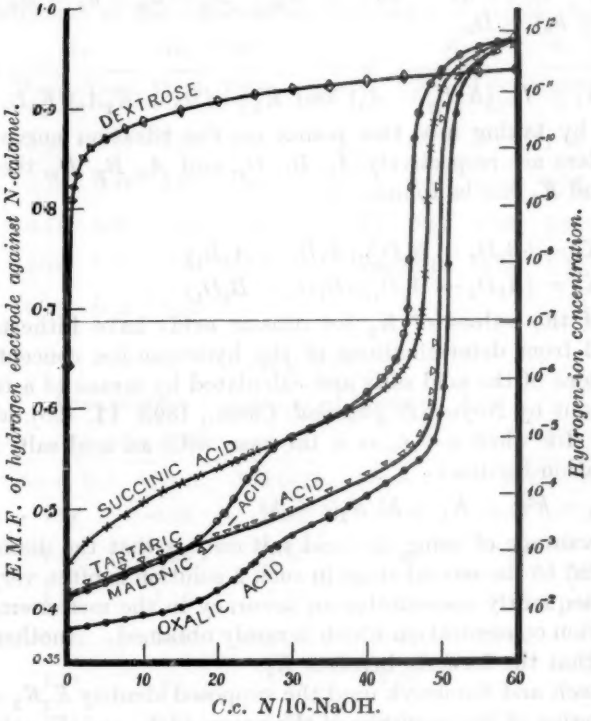
* Omitted in calculating mean.

As the solution remained appreciably alkaline throughout the titration, it was evident that some of the sodium hydroxide had remained uncombined, the concentrations of which were found from the hydrion data, and were equal to $K_w/[H^+]$, K_w at 18° being $10^{-14·14}$, if the dissociation of the alkali be assumed complete.

These concentrations are given in the fourth column, and as the combined concentrations of the sodium hydroxide and the sodium salt of dextrose were equal to the sodium concentrations produced by the added alkali, given in the fifth column, the actual concentrations of sodium glucoside were known (column 6). Then, as the concentrations of sodium glucoside were very small, it followed that these concentrations were very nearly those of the glucoside ion. Thus by knowing the concentrations of undissociated glucose, which in the circumstances were equal to those of unattacked glucose, the affinity constant was found. It will be seen that, except in the first two values, which can only be regarded as approximate in view of the rapid change in hydrion concentration which was then taking place, the values are in fairly good agreement, the average being 5·77 × 10^{-13}. The acid nature of glucose has been previously studied by Cohen (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **2**, 628) and by Madsen (*Z. physikal. Chem.*, 1901, **36**, 290), both of whom measured the rate of saponification of ethyl acetate by alkaline solutions of dextrose. From the data obtained by the former worker, Osaka (*Z. physikal. Chem.*, 1900, **35**, 673) showed that,

if dextrose be regarded as a monobasic acid, $K = 5{\cdot}9 \times 10^{-13}$, and Euler (*Ber.*, 1906, **39**, 344), using the latter's observations, obtained a value $K = 3{\cdot}6 \times 10^{-13}$ at 18°. Later, Michaelis and Rona (*Biochem. Z.*, 1913, **49**, 248), measuring the p_H values of some alkali–dextrose solutions with the hydrogen electrode, found $K = 6{\cdot}6 \times 10^{-13}$.

FIG. 1.



Calculation of the Dissociation Constants of Dibasic Acids from Titration Curves.

The following equations are based on the mass law and apply to solutions which are so dilute that the sodium salts may be taken as completely dissociated. The equations, however, differ from those of Auerbach and Smolczyk (*loc. cit.*) in that no approximations have been introduced.

Let c = the total concentration of acid, a = total concentration of added alkali, and h = hydrogen-ion concentration. A dibasic acid, H_2R, dissociates thus:

(i) $H_2R \rightleftharpoons H^{\cdot} + HR'$ (ii) $HR' \rightleftharpoons H^{\cdot} + R''$,

such that $K_1 = h[HR']/[H_2R]$ and $K_2 = h[R'']/[HR']$. Then $[H_2R] + [HR'] + [R''] = c$ and $[HR'] + 2[R''] = a - h$. By eliminating the unknowns from these four equations, it is found that

$$K_1 = h^2(a + h)/\{K_2(2c - a - h) - (ah + h^2 - hc)\} \quad \ldots\ldots\ldots (1)$$

$$K_2 = \{h^2(a + h) + K_1(ah + h^2 - hc)\}/K_1(2c - a - h) \quad \ldots\ldots (2)$$

Putting $a_n h_n + h_n^2 - h_n c_n = A_n$, $2c_n - a_n - h_n = B_n$, and $h_n^2 (a_n + h_n) = D_n$,

then

$$K_1 = D_n/(K_2 B_n - A_n) \text{ and } K_2 = (D_n + K_1 A_n)/K_1 B_n.$$

Hence, by taking any two points on the titration curve whose parameters are respectively A_1, B_1, D_1, and A_2, B_2, D_2, the values of K_1 and K_2 can be found.

Thus

$$K_1 = (B_1 D_2 - B_2 D_1)/(A_1 B_2 - A_2 B_1) \ldots\ldots\ldots (3)$$

$$K_2 = (A_1 D_2 - A_2 D_1)/(B_1 D_2 - B_2 D_1) \ldots\ldots\ldots (4)$$

Many of the values of K_2 for dibasic acids have hitherto been obtained from determinations of the hydrogen-ion concentrations of solutions of the acid salts and calculated by means of a formula, worked out by Noyes (*Z. physikal. Chem.*, 1893, **11**, 495), identical with (2), for when $a = c$, as is the case with an acid salt, NaHR, the equation becomes

$$K_2 = h^2(c + K_1 + h)/K_1(c - h) \quad \ldots\ldots\ldots (5)$$

A disadvantage of using the acid salt only is that the dissociation of the acid to the second stage in such a solution is often very small and consequently necessitates an accuracy in the measurements of the hydrion concentration which is rarely obtained. Another drawback is that the formula involves K_1.

Auerbach and Smolczyk used the supposed identity $K_1 K_2 = h^2_{x_{a/2}}$ as a criterion of the accuracy of the values of K_1 and K_2 calculated from their formulæ. It seems hardly necessary to state that the hydrogen-ion concentrations of dilute solutions of acid salts, or of solutions undergoing titration when half the total amount of alkali has been added, are functions of the concentrations of the salts. The measurements of Drucker (*Z. physikal. Chem.*, 1921, **96**, 419) show that at 20° the p_H of solutions of potassium hydrogen tartrate varies from 3·47 in 0·025M-solution to 3·55 in 0·01M-solution and to 3·93 in 0·001M-solution. Such variations render the above relationship useless, especially when applied to Auerbach and Smolczyk's titrations in which the concentration of acid salt was 0·036M-$NaHC_4H_4O_6$ at the mid-point of the tartaric acid titration. It follows also from equation (5) that $K_1 K_2$ can be equal to h^2 only

when the expression $(c + K_1 + h)/(c - h)$ is equal to unity, *i. e.*, when $K_1 = -2h$. This condition can never be obtained, and, as the data given in this paper show, the expression rarely even approximates to 1, except where K_1 is negligibly small compared with c, as in the case of succinic acid.*

TABLE VI.

Calculation of the Dissociation Constants of Oxalic Acid.

C.c. of NaOH.	K_1. Form. 3.	K_1. Table I.	$K_2 \times 10^4$. Form. 4.	$K_2 \times 10^4$. Table I.	C.c. of NaOH.	K_1. Form. 3.	K_1. Table I.	$K_2 \times 10^4$. Form. 4.	$K_2 \times 10^4$. Table I.
5·0 / 45·0	0·20	0·17	1·31	1·29	0 / 30·0	0·17	0·19	1·26	1·05
10·0 / 40·0	0·14	0·16	1·52	1·48	0 / 40·0	0·17	0·19	1·52	1·48
15·0 / 35·0	0·15	0·22	1·45	1·36	0 / 45·0	0·18	0·19	1·31	1·29
20·0 / 30·0	0·16	—	1·26	1·05	Mean	0·17	0·18	1·34	1·38
0 / 25·5	0·17	0·19	1·05	—					

TABLE VII.

Dissociation Constants of Tartaric Acid.

C.c. of NaOH.	$K_1 \times 10^3$. Form. 3.	A. & S.	Table II.	$K_2 \times 10^5$. Form. 4.	A. & S.	Table II.
5 / 45	1·22	0·66	1·33	9·56	9·77	9·08
10 / 40	1·24	1·23	1·45	9·30	7·25	8·19
15 / 35	1·30	1·10	1·75	8·56	9·03	6·62
20 / 30	1·22	1·08	2·76	10·61	10·84	5·08
0 / 25	1·28	—	1·34	9·68	—	—
5 / 30	1·21	0·63	1·33	10·65	14·87	5·08
0 / 15	1·29	—	1·34 / 1·75	9·16	—	—
20 / 30	1·29	—	—	9·64	—	—
0 / 5	1·35	—	1·33 / 1·27	[−1·24]	—	—
40 / 50	[0·91]	—	—	9·65	—	8·19 / 9·08
Mean	1·27	0·94	—	9·65	10·35	—

* The author's attention has been directed to the following. If the supposed identity, $K_1K_2 = h^2$, be substituted in Noyes's equation, it follows that K_1 must be equal to $4K_2$. As a rule, K_1 is greater than $4K_2$, but it will be observed from the following tables that in the cases of succinic and tartaric acids, where the ratio $K_1 : K_2$ is not considerable, the product K_1K_2 is only a little greater than h^2.

Table VIII.

Dissociation Constants of Succinic Acid.

C.c. of NaOH.	$K_1 \times 10^5$. Form. 3.	A. & S.	Table III.	$K_2 \times 10^6$. Form. 4.	A. & S.	Table III.
5 } 45 }	10·20	9·31	10·51	5·40	4·82	4·74
10 } 40 }	8·33	8·14	9·23	5·00	5·00	4·67
15 } 35 }	8·70	8·61	11·29	5·23	5·23	4·39
20 } 30 }	8·20	10·10	17·84	5·85	5·84	3·54
0 } 24 }	9·90	—	9·95	3·50	—	—
0 } 15 }	9·91	—	{ 9·95 { 11·29	[2·44]	—	—
25 } 35 }	[7·65]	—	—	5·32	—	4·39
Mean	9·21	9·04	—	5·30	5·22	—

Table IX.

Dissociation Constants of Malonic Acid.

C.c. of NaOH.	$K_1 \times 10^3$. Form. 3.	A. & S.	Table IV.	$K_2 \times 10^6$. Form. 4.	A. & S.	Table IV.
0 } 45 }	1·96	—	2·16	3·83	—	3·83
5 } 40 }	1·81	0·89	1·82	4·82	4·80	4·80
10 } 35 }	2·10	1·45	2·12	5·46	5·49	5·43
15·0 } 30·1 }	2·10	1·70	2·15	4·67	4·67	4·56
20 } 25 }	1·99	1·81	2·24	4·51	4·70	3·63
0 } 23 }	2·16	—	2·16	3·19	—	—
Mean	2·02	1·46	2·11	4·41	4·92	4·45

Table VI gives the values of the dissociation constants of oxalic acid calculated from the data of pairs of typical points on the titration curve from equations (3) and (4). The values recorded in Table I for the appropriate stages of the titration are also given for comparison. Auerbach and Smolczyk did not use their formula for oxalic acid, as they considered it to be too strong an acid. In Tables VII, VIII, and IX, the values of K_1 and K_2 are given for tartaric, succinic, and malonic acids respectively, as calculated from formulæ (3) and (4), also from those of Auerbach and Smolczyk, together with the comparable values already given in Tables II to IV.

Discussion.

It will be seen from Tables I and VI that the first stage of dissociation of oxalic acid is that of a strong acid and consequently does not rigidly obey the mass law. Chandler (*J. Amer. Chem. Soc.*, 1908, **30**, 705), however, found by the conductivity method that K_1 at 25° was equal to $3{\cdot}8 \times 10^{-2}$, and Drucker (*Z. physikal. Chem.*, 1920, **96**, 381) obtained a mean value $5{\cdot}7 \times 10^{-2}$ at 18°, the actual values varying from $5{\cdot}2$ to $8{\cdot}3 \times 10^{-2}$. The values of K_1 given in Table IV are much higher than these and, as Table I shows, correspond to a degree of dissociation of 0·89. For the value of K_1 to have been that obtained by Drucker, the *P.D.* for the free acid should have been 4 millivolts greater. The *E.M.F.* here recorded has, however, been obtained repeatedly. The values of K_1 given in Tables I and VI are fairly concordant over the first part of the titration, but, as Table I shows, α began to increase after 10 c.c of alkali had been added, due to the appearance of hydrions from the second stage of ionisation. The values of K_1, 0·15 and 0·16, calculated by means of equation (3) from the respective pairs of points, 15, 35 and 20, 30, show that a part only of the change in hydrion concentration thereafter was due to dissociation in the first stage.

The values of K_2 for oxalic acid calculated by the two methods at the different stages of the titration are in good agreement, although the value $1{\cdot}05 \times 10^{-4}$ obtained at 30 c.c. (Table I) is somewhat low. The value of K_2 obtained from the points 0 and 25·5 is also low, and it is at this point that equation (4) becomes, in effect, the well-known Noyes equation. The values of K_2 found in the later stages of the titration show a tendency to increase, which is no doubt largely due to the neglected ionisation of the acid and normal salts formed. The first four low values of K_2 given in Table I for the first part of the second half of the titration appear to be due to the fact that all the ions arising from the first stage of dissociation had not been neutralised. The last two values of K_2 in Table I are merely approximate, for, as the curve shows, they refer to a stage in the titration during which an exceedingly rapid change in hydrogen-ion concentration was taking place. From the values of the constants K_1 and K_2 given in Tables I and VI it will be seen that at the beginning of the titration the first dissociation only came into play, in the middle portion, represented in the diagram by the inflexion, both stages of dissociation were affected, and in the last third of the titration the second stage of dissociation alone functioned.

The average value of K_1 for oxalic acid is 0·17 and of K_2, $1{\cdot}34 \times 10^{-4}$, and therefore $K_1 = 1269\ K_2$. Chandler obtained values of K_1 ranging from $840K_2$ to $1087\ K_2$; and Drucker's values of K_2

ranged from 1·5 to 9×10^{-5}, the average value being $6·9 \times 10^{-5}$, and thus $K_1 = 825K_2$, the actual values ranging from $3800K_2$ to $650K_2$. The value now found for K_2 is thus somewhat higher than the value obtained hitherto, but it does account for the changes in hydrion concentration which take place during the process of neutralisation within narrow limits. The great difference in the two dissociation constants explains why they may be calculated in the manner adopted in Table I from the data given in the first and the last stage of the titration.

The data given in Table VII for the dissociation constants of tartaric acid calculated from formulæ (3) and (4), and from those of Auerbach and Smolczyk, show that more consistent values are obtainable from the former equations. Several values have been calculated by means of the equations given in this paper for which no corresponding values from Auerbach and Smolczyk's formulæ have been given, their formulæ having been designed for pairs of points, one on each side of the mid-point. The values of K_1 give a mean of $1·27 \times 10^{-3}$ when calculated from equation (3) and $0·94 \times 10^{-3}$ by Auerbach and Smolczyk's formula, and $K_2 = 9·65 \times 10^{-5}$ and $10·35 \times 10^{-5}$ by the respective methods. Taking K_1 and K_2 as $1·27 \times 10^{-3}$ and $9·65 \times 10^{-5}$ respectively, $K_1 = 13K_2$, and thus it becomes clear why the points 0 and 15 could be employed to calculate the value of K_2, as an appreciable quantity of the normal salt must have then been formed. The last two sets of data show that the extent to which the change in p_H between the points 0 and 5 was governed by K_2, and between the points 40 and 45 by K_1, was so small that satisfactory values of the respective constants could not be calculated.

Auerbach and Smolczyk found from their curve, $K_1 = 8·96 \times 10^{-4}$ and $K_2 = 7·46 \times 10^{-5}$ at 20°, and therefore $K_1 = 12K_2$. Other workers have found for K_1, $9·7 \times 10^{-4}$ at 25° (Ostwald, *Z. physikal. Chem.*, 1889, **3**, 369; Walden, *ibid.*, 1891, **8**, 483) and $1·17 \times 10^{-3}$ (Drucker, *ibid.*, 1920, **96**, 382), and the values of K_2 range from 2·9 to $6·9 \times 10^{-5}$ (Smith, *ibid.*, 1898, **25**, 260; Wegscheider, *Monatsh.*, 1902, **23**, 635; McCoy, *J. Amer. Chem. Soc.*, 1908, **30**, 694; Datta and Dhar, J., 1915, **107**, 824; Paul, *Z. Elektrochem.*, 1915, **21**, 552; 1917, **23**, 70; *Z. physikal. Chem.*, 1924, **110**, 417; Drucker, *loc. cit.*; Larsson, *Z. anorg. Chem.*, 1922, **125**, 281). The values of K_1 given in Table II are approximately true for the first three readings, and the highest values of K_2 are a little lower than the actual value.

There seems to be little difference between the respective values of K_1 and K_2 for succinic acid (Table VIII) as calculated by the two methods. The values based on the assumptions made in Table III

for the first part of the titration, even in the initial stages, appear to be somewhat too high, and those for the main portion of the second stage of the titration to be a little too low. The values obtained for the middle part of the titration are erratic. Excluding the values of K_1 and K_2 given in brackets in Table VII, which were obtained from pairs of points each lying in the extreme halves of the curves, $K_1 = 9{\cdot}21 \times 10^{-5}$ and $K_2 = 5{\cdot}30 \times 10^{-6}$ and therefore $K_1 = 17K_2$; and it happens that the mean values given by Auerbach and Smolczyk's formulæ give the same relationship. Auerbach and Smolczyk obtained from their titration data at 20° $K_1 = 6{\cdot}86 \times 10^{-5}$ and $K_2 = 3{\cdot}97 \times 10^{-6}$, whereas previous workers have found $K_1 = 6{\cdot}55 \times 10^{-5}$ at 25° (Ostwald, *Z. physikal. Chem.*, 1889, **3**, 272; White and Jones, *Amer. Chem. J.*, 1910, **44**, 197) and values for K_2 ranging from $2{\cdot}2$ to $4{\cdot}3 \times 10^{-6}$ (Noyes, *Z. physikal. Chem.*, 1893, **11**, 495; Smith, *loc. cit.*; Datta and Dhar, *loc. cit.*; Chandler, *loc. cit.*; Larsson, *loc. cit.*). The data of Chandler show a variation in the ratio of K_1 to K_2 from 15·5 to 26·6.

Contrary to the good agreement between the values for K_1 for succinic acid obtained by the two methods of calculation, Table IX, referring to malonic acid, shows that whereas concordant values are given by equation (3) and Table IV, the values calculated from Auerbach and Smolczyk's formula are low and increase as the points from which they were calculated approach the mid-point of the curve. The values of K_2, however, found by each of the three methods are in good agreement. Taking $K_1 = 2{\cdot}02 \times 10^{-3}$ and $K_2 = 4{\cdot}41 \times 10^{-6}$, it follows that $K_1 = 476K_2$, as compared with Chandler's results at 25°, which show a variation of K_1 from $357K_2$ to 493 K_2 when the latter constant was determined by McCoy's partition method, whereas K_1 is given as $1{\cdot}58 \times 10^{-3}$, which was also obtained by Ostwald (*loc. cit.*), and K_2 as $2{\cdot}1 \times 10^{-6}$, from conductivities, and thus $K_1 = 752K_2$. Other values are: K_1, $1{\cdot}61 \times 10^{-3}$ at 25° (White and Jones, *loc. cit.*) and K_2, $1{\cdot}41 \times 10^{-6}$ at 25° (Datta and Dhar, *loc. cit.*).

It was mentioned on p. 1904 that Auerbach and Smolczyk used the expression $K_1K_2 = h^2$, where h was the hydrogen-ion concentration at the point of half neutralisation, and this could only be true if $(c + K_1 + h)/(c - h)$ in the expression $K_2 = h^2 (c + K_1 + h)/K_1(c - h)$ was equal to unity. Putting $\lambda = (c + K_1 + h)/(c - h)$, then $K_1K_2 = \lambda h_2$.

Table X gives the values of λ as calculated from (*a*) the data obtained at the mid-points of the titrations, the mean values of K_1 obtained from formula (3) being used, (*b*) the products K_1K_2 divided by h^2, the constants having been calculated from equations (3) and (4), λ_D, and (*c*) the products K_1K_2 divided by h^2, the constants used

being those found by Auerbach and Smolczyk's formulæ, λ_A. The numbers given in brackets show the variations in the products and the corresponding changes produced in the values of λ.

TABLE X.

			Form. 3 and 4.		A. & S.'s form.	
Acid.	h^3.	λ.	K_1K_2.	λ_B.	K_1K_2.	λ_A.
Oxalic	$1{\cdot}76\times10^{-6}$	10·1	$2{\cdot}28\times10^{-5}$	13·0	—	—
			(1·83—2·52)	(10·4—14·3)		
Tartaric	$1{\cdot}13\times10^{-7}$	1·10	$1{\cdot}23\times10^{-7}$	1·09	$0{\cdot}97\times10^{-7}$	0·86
			(1·11—1·29)	(0·98—1·14)	(0·64—1·17)	(0·57—1·04)
Succinic	$3{\cdot}44\times10^{-10}$	1·01	$4{\cdot}88\times10^{-10}$	1·42	$4{\cdot}72\times10^{-10}$	1·37
			(3·46—5·50)	(1·01—1·60)	(4·07—5·91)	(1·18—1·72)
Malonic	$6{\cdot}11\times10^{-9}$	1·12	$8{\cdot}90\times10^{-9}$	1·45	$7{\cdot}18\times10^{-9}$	1·17
			(6·89—11·46)	(1·13—1·87)	(4·27—8·51)	(0·70—1·39)

It is evident from the table that only in the case of succinic acid does $\lambda = 1$; the expression $(c + K_1 + h)/(c + h)$ shows that this can be so only when K_1 is exceedingly small and h has become correspondingly small, such as happens to be the case with succinic acid. For the other acids, both K_1 and h are sufficiently large compared with c to render λ appreciably greater than 1, the extreme case being that of oxalic acid, for which $\lambda = 10$. The values of λ_B, whilst being of the same order as λ, show some variations which are due largely to the neglect of the ionisation of the salts formed during the titrations. The values of λ_A show similar, although somewhat greater variations, and these are caused by errors due both to dissociation and to the fact that the Auerbach–Smolczyk formulæ do not yield satisfactory results for K_1 when it happens to be fairly large, *e. g.*, of the order of 10^{-3}.

By an approximate mathematical analysis Auerbach and Smolczyk have shown how the character of the titration curves is determined by the ratio of their dissociation constants. Thus when K_1 is greater than $16K_2$ the curve will have an inflexion in the middle, whereas when $K_1 = 16K_2$ the curve will be a straight line, and when K_1 is less than $16K_2$ the curve will be similar to that of a monobasic acid. The curves of oxalic and malonic acids, the second dissociation constants of which are considerably less than $1/16K_1$, *viz.*, 1/1269 and 1/476 respectively, have each large inflexions (Fig. 1), whereas in that of succinic acid an exceedingly small inflexion is perhaps just discernible, and the curve for tartaric acid ($K_1 = 13K_2$) is straighter.

It is striking that the first two members—oxalic acid and malonic acid—of the saturated dibasic acid series,

$$HO_2C{\cdot}[CH_2]_n{\cdot}CO_2H,$$

should exhibit such a great difference in their two dissociation

constants, in each case the first constant being several hundred times the second, as compared with the next member, succinic acid, the first constant of which is only seventeen times the second. The dissociation constants found by Chandler (*J. Amer. Chem. Soc.*, 1908, **30**, 713) for the remaining members of the series up to sebacic acid, $n = 8$, reveal the remarkable fact that the values of K_2 from malonic acid upwards are all approximately equal and of the order 10^{-6}, and that there is only a small diminution in K_1 of the ascending acids of the series, but they are all of the order given by succinic acid, *viz.*, 10^{-5}. Hence the titration curves of these acids will be similar to that of succinic acid and, in fact, almost coincident with it.

The views relating to the acidity of dibasic acids held at the present time appear to be those which were first enunciated by Ostwald (*Z. physikal. Chem.*, 1892, **9**, 553) and are based on the electrostatic charges carried by the various ions and the influence that may be exerted by virtue of the proximity of the carboxyl groups. He considered that in the ionisation of a dicarboxylic acid the negative charge carried by the anion, arising from the first dissociation, exerted a force of repulsion on the negative charge carried by the other carboxyl group and that the nearer one carboxyl group was to the other the greater would be this repulsive force, which would therefore tend to prevent the ionisation proceeding to the second stage.

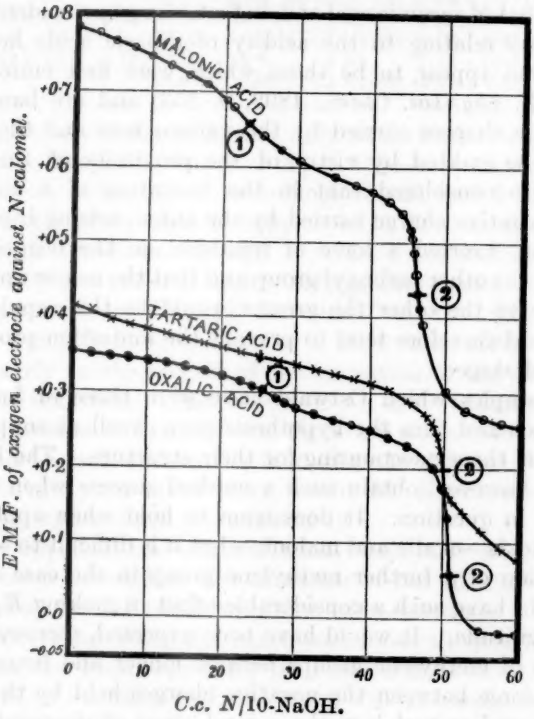
The examples which Ostwald gave were those of fumaric and maleic acids and thus the hypothesis gave excellent support to the van 't Hoff theory accounting for their structure. The hypothesis does not, however, obtain such a marked success when applied to the series in question. It does seem to hold when applied to the first two acids—oxalic and malonic—but it is difficult to see why the interposition of a further methylene group in the case of succinic acid should have such a considerable effect in making K_1 approach K_2 in magnitude. It would have been expected, moreover, that as the chain of methylene groups became longer and longer and the repulsive force between the negative charges held by the carboxyl groups grew less and less, the second stage of dissociation would have become greater and greater, gradually becoming equal to the very slowly decreasing K_1, instead of remaining unchanged.

Part II. *Oxygen Electrode Titrations.*

For the purpose of examining more closely the behaviour of the oxygen electrodes during titrations, three of the acid solutions titrated with the hydrogen electrode were chosen, for their titrations involved changes in hydrogen-ion concentrations which extended over the whole acid zone. 100 C.c. each of 0·0230*M*-malonic acid,

0·0250*M*-tartaric acid, and 0·0255*M*-oxalic acid were titrated at 18° with *N*/10-sodium hydroxide, the oxygen electrode being used in the way outlined in an earlier paper (Britton, J., 1924, **125**, 1572). Observations were made similar to those in the titrations of chromic acid (*loc. cit.*) regarding the initial *E.M.F.*'s, which were again independent of the nature of the acid, and to some extent independent of the initial hydrogen-ion concentration of the solution. As a rule, no two oxygen electrodes ever gave the same *E.M.F.*'s

FIG. 2.



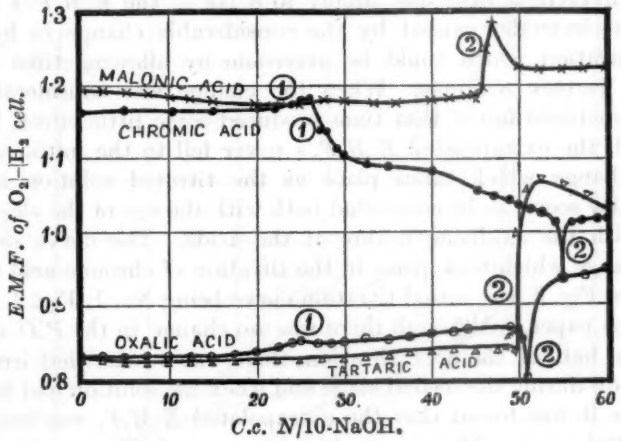
when immersed in the same solution. Typical titration curves are given in Fig. 2, the ordinates being the observed *P.D.*'s between the oxygen electrode and the normal calomel electrode, and the abscissæ the amount of alkali added. The three titrations were made on successive days with the same electrode, of the Hildebrand type but having a platinised platinum wire instead of foil, and were carried out in the order malonic, tartaric, and finally oxalic acid. As the electrode became more and more aged, the *E.M.F.* readings became less positive. The electrodes also tended to become more

and more erratic after having been subjected to rapid changes in hydrion concentration.

Comparison of Oxygen and Hydrogen Electrode Curves.

In the previous paper it was pointed out that, if the oxygen electrode behaved ideally, the algebraic differences between the *E.M.F.*'s given by the oxygen electrode and by the hydrogen electrode at comparable stages of a titration should remain constant, these differences being the *P.D.*'s of the oxygen–hydrogen cell in the various solutions. These differences have been ascertained for each of the three titrations and are plotted in Fig. 3.

FIG. 3.



The *E.M.F.*'s of the oxygen–hydrogen cell extrapolated from the titration curves of the three organic acids show that in the case of malonic acid there was a gradual but small diminution until the first equivalent had been neutralised, after which the *P.D.* remained constant until the end-point had been reached; it then suddenly increased, but afterwards fell to a value somewhat higher than the initial *E.M.F.* The oxalic and tartaric acid titrations, which were performed with electrodes which had become a little aged, produced small and gradual increases in *P.D.* apart from the slight inflexion which occurred at the mid-point of the oxalic acid curve due to a lag in the *E.M.F.* of the oxygen electrode, until the neutralisation was complete; the *E.M.F.* of the oxygen–hydrogen cell then suddenly increased and thereafter remained constant in the case of the oxalic acid curve but fell somewhat for the tartaric curve. Thus in these three titrations the extrapolated *E.M.F.*'s of the oxygen–

hydrogen cell were greater at the end of the titration than at the beginning; the actual values are given in Table XI.

TABLE XI.

Acid.	*E.M.F.* of oxygen–hydrogen cell at Beginning.	End.	Difference.
Malonic	1·195	1·228	+0·033
Tartaric	0·828	1·034	+0·206
Oxalic	0·830	0·950	+0·120
Chromic	1·162	1·027	−0·135

The curves in Fig. 3 show that the differences were not proportionally incorporated in the oxygen electrode voltages, but were included mainly in the end-point readings. It was thought that these differences were due simply to a lag in the *E.M.F.*'s of the oxygen electrodes caused by the considerable change in hydrion concentration, which could be overcome by allowing time before taking further readings. When the change was considerable, it was sometimes found that time produced some little effect, but in general, the extrapolated *E.M.F.*'s never fell to the initial values. This change which takes place as the titrated solution attains alkalinity seems to be connected both with the age of the electrodes and with the oxidising nature of the acids. The curve showing the change which took place in the titration of chromic acid is also given in Fig. 3, the actual titration curve being No. 1, Fig. 2, in the previous paper. Although there was no change in the *P.D.* during the first half of the neutralisation, there was a somewhat irregular falling off during the second stage and when the solution had become alkaline it was found that the extrapolated *E.M.F.* was less than the initial value. This occurred in every one of the many titrations undertaken. The hydrogen-ion concentration prevailing during the second half of the titration lay between 10^{-6} and 10^{-7} and it seems that it was here and later in the alkaline solution that the oxidising nature of the chromic acid came into play. No irregularities occurred with the non-oxidising acids dealt with in this paper and especially with malonic acid, the second part of the neutralisation of which was not far removed from the neutral point.

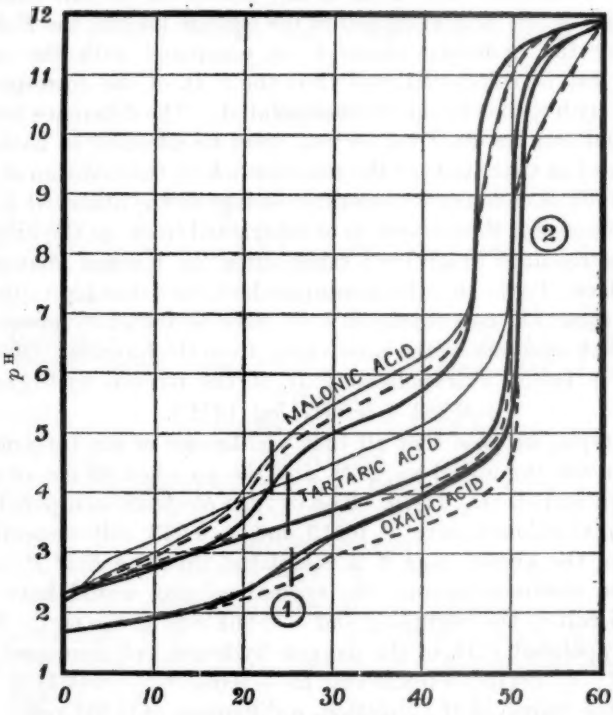
Calibration of the Oxygen Electrode in Titrations.

The erratic behaviour of the oxygen electrode whilst being subjected to rapid changes in hydrion concentration, such as shown in Fig. 3 to take place at the end-points of titrations, renders it almost impossible to affix a satisfactory hydrogen-ion concentration scale to the measured voltages. It is possible, however, to get an approximate idea of the changes in p_H over the greater range of the

titration, for which purpose the following two schemes of calibration have been examined.

First, knowing the p_H's of solutions at two remote stages of a titration and the corresponding voltages given by the oxygen electrode, one assumes that the intermediate p_H's are proportional to the observed *E.M.F.*'s. In Fig. 4, the p_H curves of the three organic acids obtained with the hydrogen electrode are given as heavy lines

FIG. 4.



C.c. $N/10$-NaOH.

and the thin line lying near to each one of them is the curve calculated from the oxygen electrode titration voltages. It will be seen that the p_H's given by the malonic acid curve are higher by about 0·5 unit, due to a lag of 0·033 volt being divided proportionally over the p_H range of the titration, whereas the lag of 0·206 volt shown by the tartaric acid curve causes the oxygen curve to lie higher on the diagram, in some places nearly a whole p_H unit, and yet in the case of oxalic acid, with its lag of 0·120 volt, the oxygen curve is almost coincident with the hydrogen curve, save for a small deviation in the middle section. This is due to the gradual increase in the

extrapolated *E.M.F.* which took place throughout the acid zone of the oxalic acid titration.

The second method of calibration was based on the fact, illustrated by Fig. 3, that the oxygen electrode voltages are more positive than the corresponding hydrogen electrode voltages by approximately a fixed amount, when working over a range of hydrion concentration which does not involve sudden changes, and that the appreciable variations occur only when a very sharp change in hydrion is encountered. Thus in any one of the present titrations, if the p_H's at the beginning and at the end are known, the *E.M.F.*'s given by the hydrogen electrode as compared with the normal calomel can be calculated, and thus the *P.D.* of the corresponding oxygen–hydrogen cells can be extrapolated. The difference between the initial and the final values may then be assumed to have been introduced at that stage of the titration where the addition of a few drops of alkali caused a considerable change in the observed *E.M.F.* This difference is then added to or subtracted from, as the case may be, those readings which were taken after the marked change had taken place. To the titration readings which have thus been adjusted, the hydrogen-ion concentration scale may be found by proportion, or by what amounts to the same thing, from the formula: Observed *E.M.F.* = Initial extrapolated *P.D.* of the oxygen–hydrogen cell

$$+ 0{\cdot}283 + 0{\cdot}0577 \log 1/[H^{\cdot}].$$

For example, suppose that all that was known of the tartaric acid titration was the initial p_H, 2·29, and the p_H when 60 c.c. of alkali had been added, *viz.*, 11·75. The oxygen electrode compared with the normal calomel gave + 0·413 and + 0·073 volt respectively, and from the known p_H's it is calculated that the *E.M.F.* of the hydrogen electrode against the normal calomel would have been − 0·415 volt at the beginning and − 0·961 volt at the end. Hence the extrapolated *P.D.* of the oxygen–hydrogen cell increased from + 0·413 −(−0·415) = 0·828 volt to + 0·073 − (− 0·961) = 1·034 volt in the course of the titration, a difference of 0·206 volt. This is a considerable quantity to be divided proportionally over the whole titration as was done in the first method of calibration, and consequently would produce a very unsatisfactory hydrion scale. But, as Fig. 3 shows, the greater part of this difference was introduced at the end-point. Therefore, if the difference 0·206 volt be added to each of the voltages observed after the end-point had been passed and then either a proportional scale be affixed or calculated from $E = 0{\cdot}828 + 0{\cdot}283 + 0{\cdot}0577 \log 1/[H^{\cdot}]$, a more satisfactory calibration is obtained, save for that part of the curve corresponding to the initial alkaline solutions. The curves obtained by this procedure are given by dotted lines in Fig. 4. The tartaric acid